

REACTIONS OF PHOSPHORUS (III) REAGENTS

WITH NITRO COMPOUNDS AND NITROXYLS

by

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I should like to thank Professor Cadogan for stimulating my initial interest in the research topic, and for his advice and encouragement throughout the course of the work.

I also wish to thank Dr. Alan Rowley for his kind support and fruitful discussions. Many other colleagues and members of staff at Edinburgh are due my thanks, but special mention must be made of Dr. Mark Edwards, with whom I had many stimulating conversations, and Mr. Tom Naisby, who provided invaluable practical advice and assistance.

Mrs. C. Ranken has made my task much easier by her excellent typing.

Declaration

I declare that this thesis is my own composition, that the work of which it is a record was carried out by myself, and that it has not been submitted in any previous application for a Higher Degree.

The thesis describes results of research carried out in the Department of Chemistry, University of Edinburgh under the supervision of Professor J. I. G. Cadogan since the 1st October 1974, the date of my admission as a research student.

The following courses have been attended: Organic Chemistry Seminars, Edinburgh University Chemistry Department (3 years attendance); Molecular Rearrangements (5 lectures), Dr. G. Tennant; High Speed Liquid Chromatography (5 lectures), Professor J. H. Knox and Dr. J. Done; Petrochemical Research (5 lectures), members of B. P. research group; Biomimetic Organic Chemistry (5 lectures), Dr. R. M. Paton; Organic Phosphorus Compounds in General Synthesis (5 lectures), Professor J. I. G. Cadogan and Dr. I. Gosney; Organic Sulphur Compounds in General Synthesis (5 lectures), Dr. D. Leaver.

A report on some aspects of this work has been published:-

"The Reactivity of Organophosphorus Compounds. Part 33. Formation of Stable 3,4-Diaryl-4,5-dihydro-2-oxo-1,2,5-oxazaphosph(v)oles by Reaction of 1,2-Diaryl-1-nitroethenes with Phosphorus(III) Esters," by J. I. G. Cadogan, Robert A. North, and Alan G. Rowley, J. Chem. Research (S), 1978, 1; (M), 1978, 0178-0188.

For

my mother

and Rhona, my wife

Abstract

Reactions of triethyl or trimethyl phosphite with 2-aryl-1-phenyl-1-nitroethenes at elevated temperatures gave small yields only of non-phosphorus-containing heterocyclic compounds. Observation of the reactions by n. m. r. spectroscopy, however, showed that 3,4-diaryl-4,5-dihydro-1,2,5-oxazaphosph(v)ole-2-oxides were formed, and subsequently decomposed, under the reaction conditions. The use of t-butanol as solvent for the reaction enabled a range of novel 4,5-dihydro-1,2,5-oxazaphosph(v)ole-2-oxides to be prepared and isolated at room temperature. The reaction was extended by the use of dimethyl phenylphosphonite and 2-phenyl-1,3,2-dioxaphospholan, instead of trialkyl phosphites.

Further investigations, of the thermolysis of the 1,2,5-oxazaphosph(v)ole-2-oxides and their reactions with tervalent phosphorus reagents, suggested that the compounds were not intermediates in the formation of the non-phosphorus-containing heterocycles isolated previously. The results suggested that the reaction of a tervalent phosphorus reagent with a 2-aryl-1-phenyl-1-nitroethene involves two competing pathways:- Michael-type addition of the phosphorus reagent to the nitroethene, with the possibility of subsequent ring-closure to give a 4,5-dihydro-1,2,5-oxazaphosph(v)ole-2-oxide, or deoxygenation of the nitro-group to give a vinyl nitrene, and hence nitrene-derived products.

The thermolyses of two aryl 2-azidophenyl ethers in triethyl phosphate were found to give significantly different yields of products than the corresponding reactions in decalin. The possible formation of a zwitterionic nitrene-phosphate adduct as a reactive intermediate seems to be insufficient explanation of the observed results.

Reaction of N-t-butylphenylnitroxyl and diphenylnitroxyl with triethyl phosphite, in ethanol or methanol saturated with lithium chloride, gave ring-chlorinated anilines. This was taken as evidence in support of a reaction mechanism in which pairs of aminyl radicals undergo an

electron-transfer reaction to give an anilino-anion and a delocalised nitrenium ion, which readily undergoes nucleophilic aromatic substitution by the solvent or chloride ion.

The decomposition of 1,4-di-t-butyl-1,4-bisphenyltetraz-2-ene in ethanol or methanol also gave ring-substituted N-t-butylanilines.

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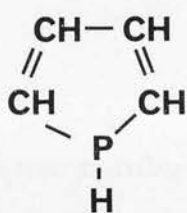
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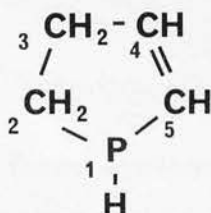
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A Note on Nomenclature

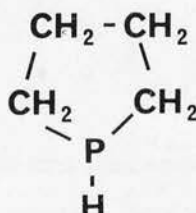
Compounds in which a phosphorus atom is incorporated in a ring are named following the general rules for heterocyclic compounds (Hantzsch-Widman). For example, the names of structures (a), (b), and (c) are, respectively, phosphole, 2, 3-dihydrophosphole, and phospholan.



a

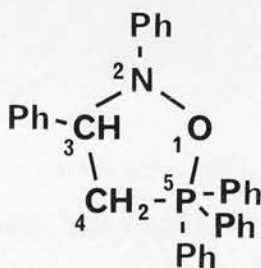


b



c

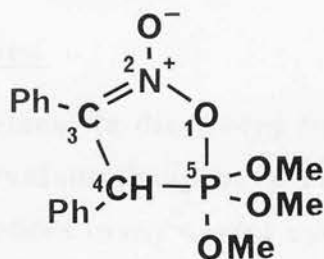
In these cases the prefix "phosph" indicates the type of heteroatom, the stem "-ole" indicates a five-membered unsaturated system [qualified by "2, 3-dihydro-" in example (b)], and the stem "-olan" indicates a five-membered saturated system. The stem "-olan" is replaced by "-olidine" when a nitrogen atom is incorporated in the five-membered saturated ring, e. g. 2, 3, 5, 5, 5-pentaphenyl-1, 2, 5-oxazaphosph(v)olidine (d).



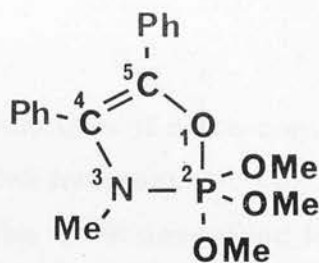
d

In monocyclic compounds, when other heteroatoms in addition to phosphorus are incorporated in the ring, the locant 1 is assigned to the heteroatom of highest priority. The decreasing order of priority, which also determines the listing of prefixes, is O>S>N>P. Numbering of the ring is then continued so as to assign the lowest possible locants to the remaining heteroatoms, the order of priority now being a secondary consideration. Two compounds may serve as examples, 4, 5-dihydro-3, 4-diphenyl-5, 5, 5-trimethoxy-1, 2, 5-oxazaphosph(v)ole-2-oxide (e) and

2, 3-dihydro-4, 5-diphenyl-3-methyl-2, 2, 2-trimethoxy-1, 3, 2-oxaza-phosph(v)ole (f).

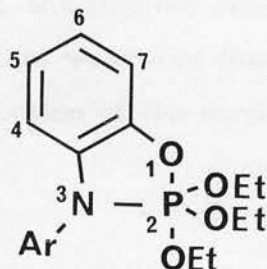


e



f

When numbering fused systems it is not necessary to assign the locant 1 to the heteroatom of highest priority, but the heteroatoms are assigned the lowest possible set of locants, with the rule of priority becoming a secondary consideration. This is illustrated for 3-aryl-2, 3-dihydro-2, 2, 2-triethoxy-1, 3, 2-benzoxazaphosph(v)ole (g).



g

The phosphorus atom can exist in the (III) or (V) oxidation state, and this may be indicated, particularly in the case of the latter, by insertion of (III) or (V) between the prefix and stem [examples (d) to (g) above].

Introduction

Foreword

Since its discovery in 1962, the reaction of nitro-compounds with tervalent phosphorus reagents to give heterocyclic compounds has provided many useful syntheses. The work described in this thesis was undertaken to shed further light on several of these reactions, but in particular on the deoxygenation of 1, 2-diphenylnitroethenes. It soon became apparent during the course of the research that the formation of comparatively stable phosphorus-containing heterocycles was a major feature of this reaction. As background to this work, the introduction consists of a review of the deoxygenation of nitro-compounds by tervalent phosphorus reagents and a survey of relevant phosph(v)ole chemistry.

In addition, the introduction reviews the deoxygenation of N-oxides and nitroxyl radicals; the former because the phospholes prepared during the course of this work are themselves N-oxides, and the latter because a separate section of the work is devoted to this recently discovered reaction.

A. Deoxygenation of Aromatic Nitro- and Nitroso-compounds by Tervalent Phosphorus Reagents

A.1 General

The study of organophosphorus chemistry made a new and significant departure in 1962 with the publication of two papers by Cadogan and his co-workers in which the reaction between triethyl phosphite and 2-nitro-¹ and 2-nitrosobiphenyl² to give carbazole and triethyl phosphate was described. The implications that these novel reactions might have more general utility in the field of heterocyclic synthesis stimulated considerable interest, so that over the next fifteen years a large number of applications of the reaction were found, and several reviews had been published.^{3, 4, 5, 6}

Earlier work, of more limited synthetic value, had shown that azoxybenzenes were formed when triphenyl phosphine reacted with substituted nitrosobenzenes,⁷ and that the reaction of 1, 2-dinitrobenzene with triphenyl phosphine⁸ gave triphenyl phosphine oxide as the only identifiable product.

The early investigations of the reaction between tervalent phosphorus compounds and nitro- and nitroso-compounds had been prompted by the knowledge that oxidation of a PR_3 species, where R may be, for example, alkyl, alkoxy, aryl, or combinations of these, was readily accomplished by a wide range of oxygen-containing compounds,⁹ including amine N-oxides,^{7, 10} (Scheme 1).



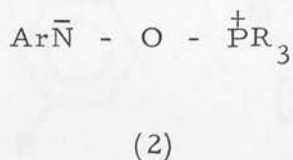
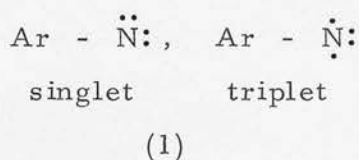
Scheme 1

The major driving force behind this change of oxidation state from P(III) to P(V) is the great strength of the P=O bond,¹¹ (500-630kJ mol⁻¹). In comparison, the bond dissociation energies for the N^+-O^- bond in amine N-oxides¹² lie in the range 210-300kJ mol⁻¹.

Sections A. 2 and A. 3 of this introduction provide a summary of the investigations of the deoxygenation of nitro- and nitroso-compounds by tervalent phosphorus reagents, illustrating the scope and limitations of the reactions and the attempts to clarify the mechanism.

A. 2 (a) Deoxygenation of Nitro- and Nitroso-benzenes, including 2-Alkyl derivatives

The mechanism of the reaction between tervalent phosphorus reagents and nitro- and nitroso-compounds in general, has been the subject of much debate.¹³ Whether the nitro-group is first reduced to nitroso, or not, and whether subsequent reaction is via a nitrene (1) or via a zwitterionic "nitrenoid" (2), are questions which have proved difficult to answer unambiguously. For the purpose of describing the reactions in



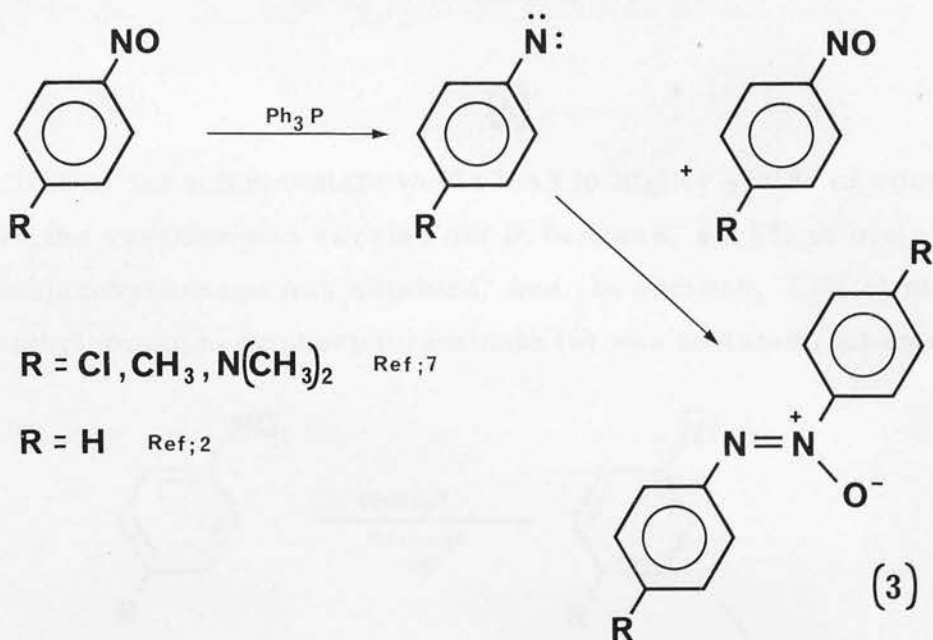
this and the subsequent sub-sections, however, a nitrene mechanism will be assumed, leaving detailed discussion of the nature of the intermediate until section A. 3.

In general, studies of the deoxygenation reactions have been carried out by dissolving the nitro- or nitroso-compound in an excess of the phosphorus reagent, or in a solvent together with an approximately stoichiometric amount of the phosphorus reagent. Nitroso-compounds react readily at room temperature, or lower, but nitro-compounds are only reduced at elevated temperatures.

Simple nitro- and nitroso-benzenes react with tervalent phosphorus reagents to give, in addition to the oxidised phosphorus compound, four major types of products; (i) products arising from the coupling of a nitrene intermediate with unreacted starting materials, (ii) products in which the nitrene has inserted, either inter- or intra-molecularly, into a C-H bond,

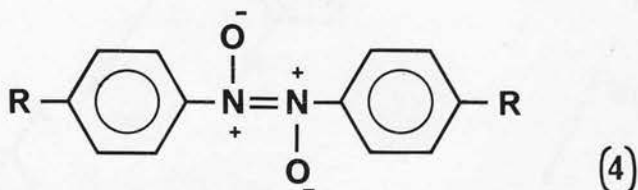
(iii) 3H-azepines formed by ring expansion of the aryl nitrene in the presence of a nucleophile, and (iv) substitution products in which a new group is attached to the benzene ring.

(i) Coupling Reactions. In 1956, Hoffmann and Horner⁷ reported that p-substituted nitrosobenzenes react with triphenyl phosphine to give ca 50% yields of the corresponding azoxybenzenes (3), (Scheme 2).



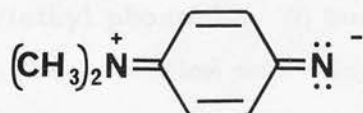
Scheme 2

Although it is possible that the azoxybenzenes were formed by deoxygenation of a nitroso dimer (4), this seems unlikely in view of the comparatively severe conditions normally required to deoxygenate N-oxides.¹⁰



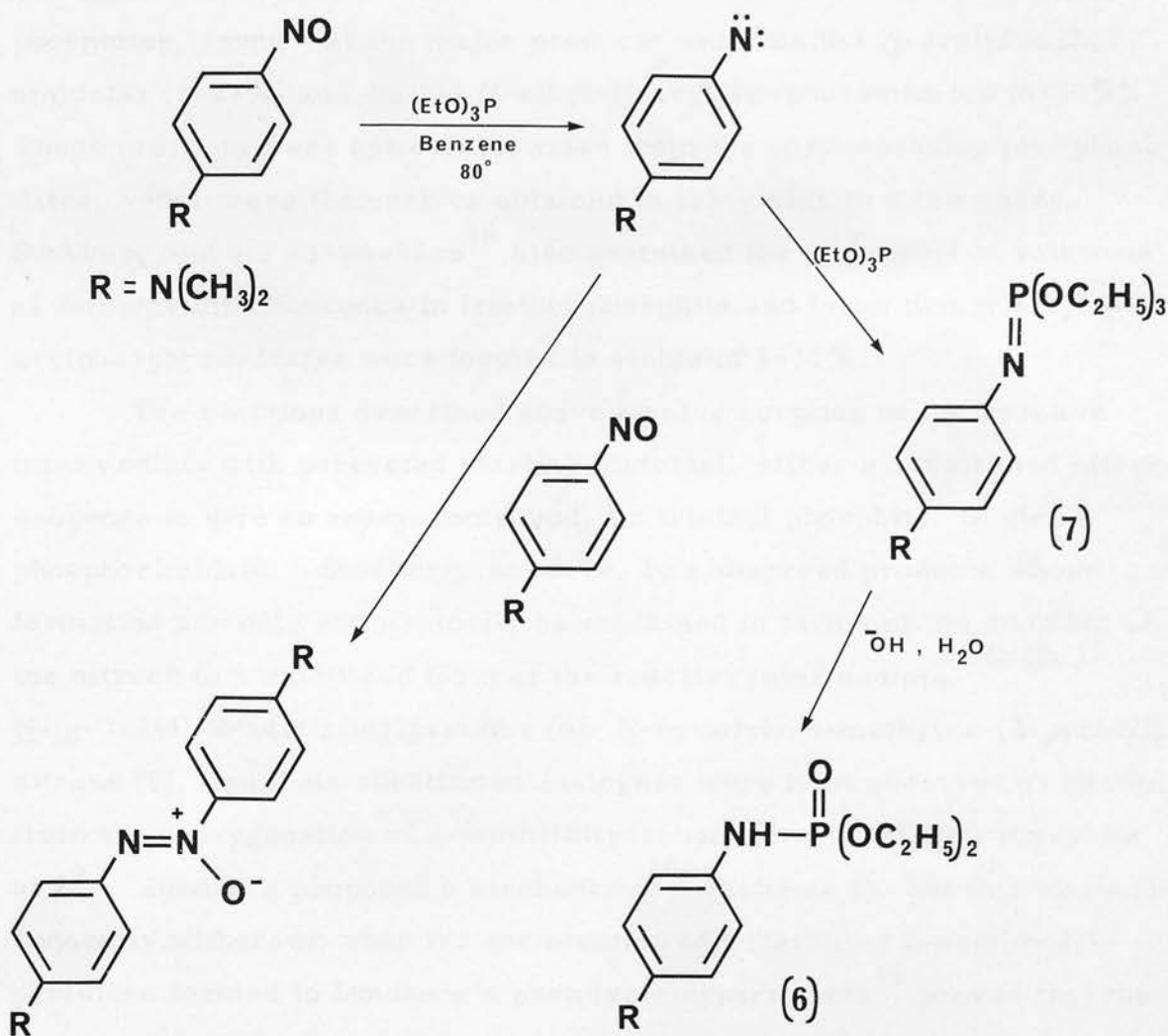
The reaction was used by Bunyan and Cadogan² to obtain azoxybenzene itself, but the yield was stated to be low. It was later reported,¹⁴ however, that carrying out the reaction in a solvent, benzene, gave azoxybenzene in

an improved yield of 21.4%. It was expected¹⁴ that deoxygenation of *p*-dimethylaminonitrosobenzene would give a more stable nitrene because of contribution from resonance form (5) and that the resulting increased



(5)

lifetime of the intermediate would lead to higher yields of coupled products. When the reaction was carried out in benzene, 63.5% of bis(*p*-dimethylamino)azoxybenzene was obtained, and, in addition, 13% of diethyl *N*-*p*-dimethylaminophenylphosphoramidate (6) was isolated (Scheme 3).



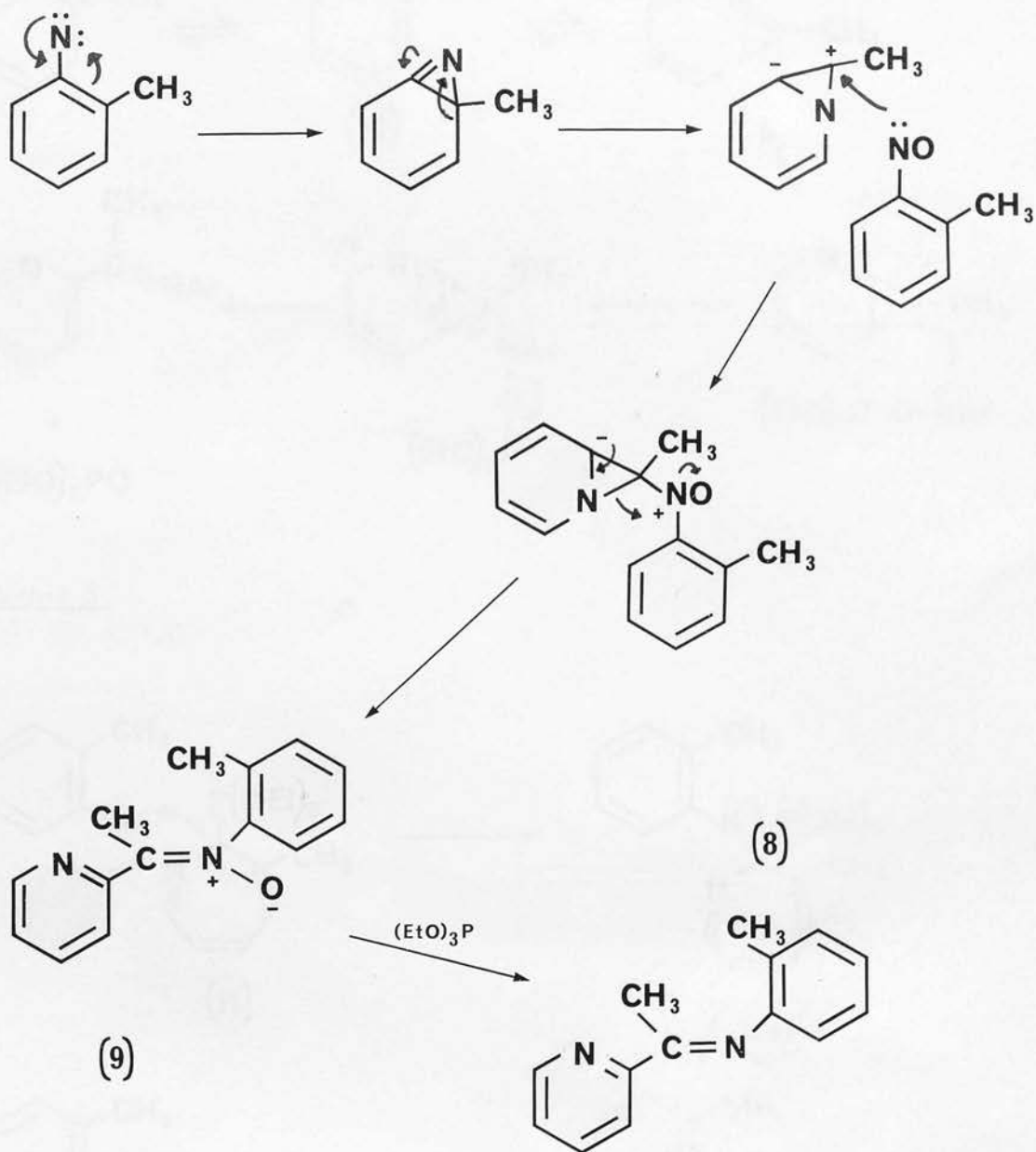
Scheme 3

Formation of the phosphoramidate (6) was explained in terms of coupling of the nitrene with triethyl phosphite, in a manner analogous to the capture of carbenes by triphenyl phosphine,¹⁵ to give triethyl N-p-methylaminophenylphosphorimidate (7), which was subsequently hydrolysed to (6) during the work-up. That a competition existed between the substituted nitrosobenzene and triethyl phosphite, to couple with the nitrene, was further indicated when the reaction was carried out in a ten-fold excess of triethyl phosphite, with no solvent, and gave 58.5% of phosphorimidate (7) and only 23% of the substituted azoxy-compound.

Derivatives of nitrobenzene also react with tervalent phosphorus reagents to give N-arylphosphorimidates and N-arylphosphoramidates.^{16, 17, 1} Sundberg¹⁶ deoxygenated 2-alkylnitrobenzenes in triethyl phosphite and found the corresponding triethyl N-arylphosphorimidates in yields of 37 to 51%. Cadogan and his co-workers,¹⁷ however, while examining the deoxygenation of a wide range of substituted nitrobenzenes by trialkyl phosphites, found that the major products were dialkyl N-arylphosphoramidates (5-27%) and dialkyl N-alkyl-N-arylphosphoramidates (8-30%). These products were believed to arise from the corresponding phosphorimidates, which were themselves obtained in low yields in a few cases. Sundberg and his co-workers¹⁸ also examined the photolysis of solutions of 2-methylnitrobenzenes in triethyl phosphite and found that triethyl N-arylphosphorimidates were formed in yields of 1-51%.

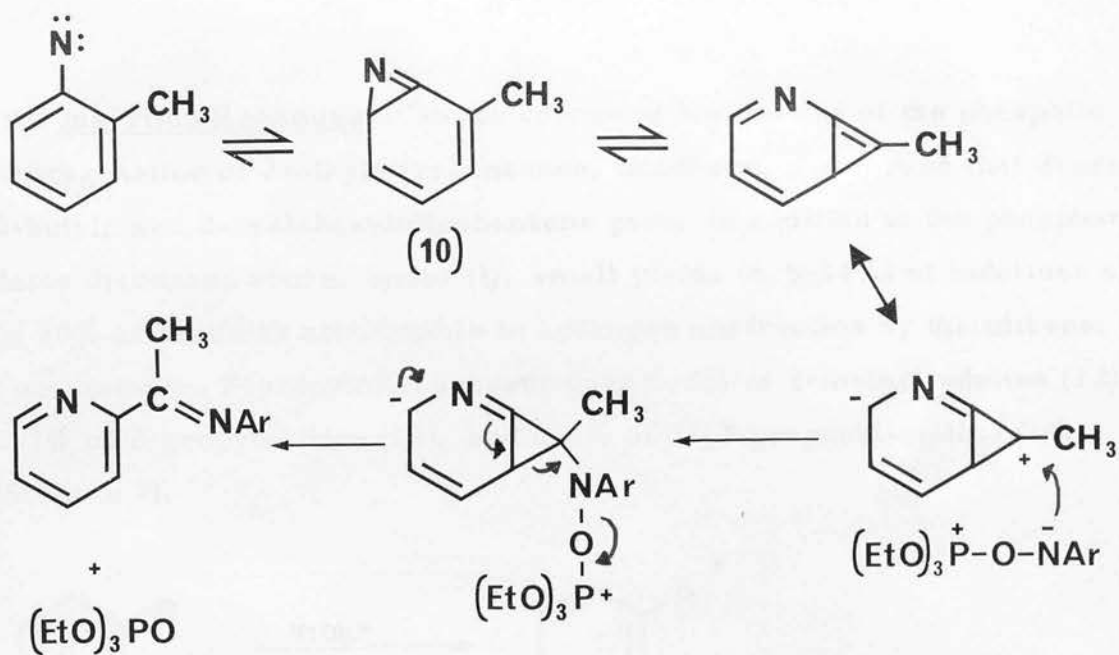
The reactions described above involve coupling of the reactive intermediate with unreacted starting material, either a substituted nitrosobenzene, to give an azoxy-compound, or trialkyl phosphite, to give a phosphorimidate. Sundberg, however, has observed products whose formation can only satisfactorily be explained in terms of the coupling of the nitrene to a stabilised form of the reactive intermediate.^{16, 18, 3}

N-(o-Tolyl)-2-acetimidylpyridine (8), N-(o-tolyl)- α -methyl- α -(2-pyridyl)-nitrene (9), and their substituted analogues were first observed as products from the deoxygenation of 2-methylnitrosobenzenes in triethyl phosphite at 0°. Sundberg proposed a mechanism^{16c} (Scheme 4), but this was subsequently withdrawn when the examination of substituted 2-acetimidylpyridines formed in Sundberg's photolysis experiments¹⁸ proved that the

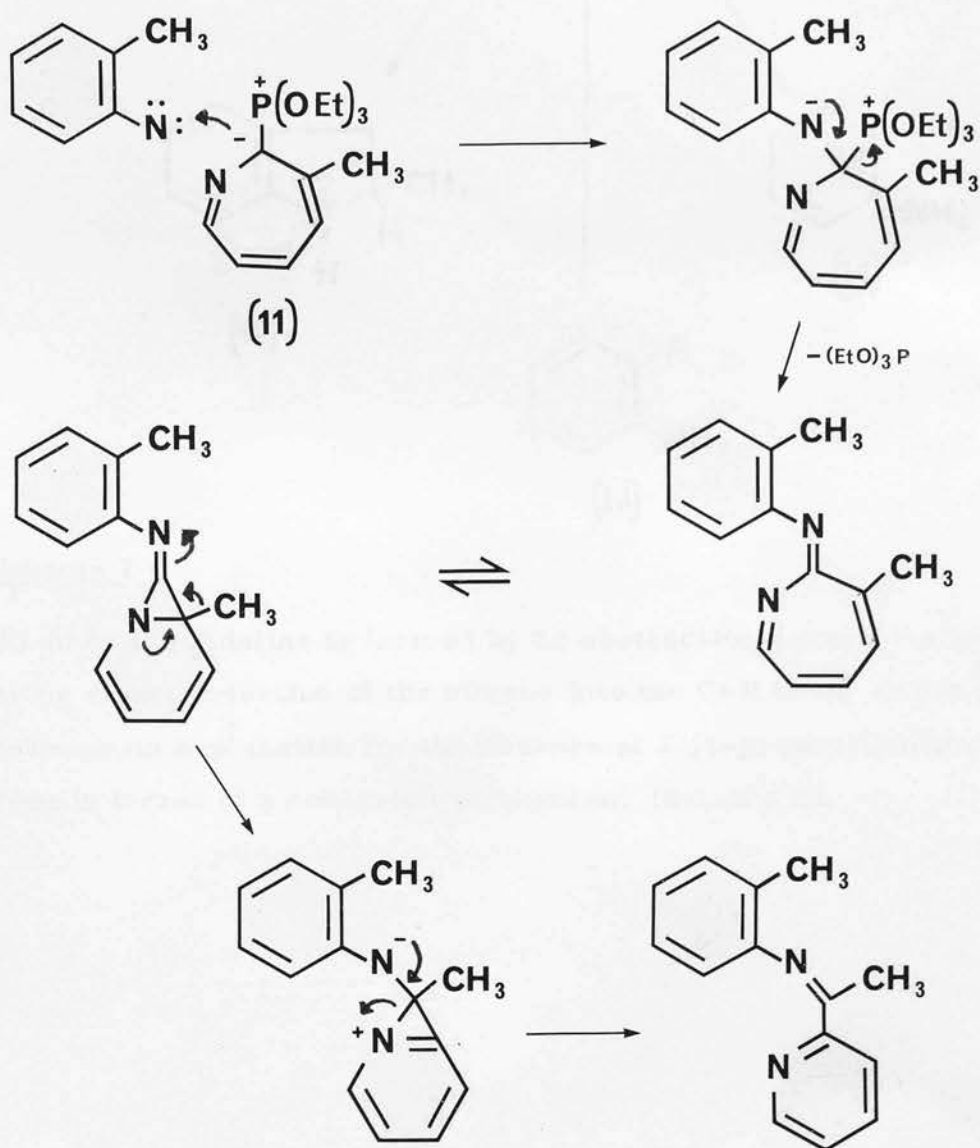


Scheme 4

skeletal rearrangement was more complex than previously thought. Two tentative suggestions of mechanism, by Cadogan³ (Scheme 5) and Sundberg^{18b} (Scheme 6), have been made. The postulations of an azirine intermediate (10) and an azepinyl intermediate (11) arise out of attempts to explain the formation of 3H-azepines under certain conditions, as discussed below, under (iii).

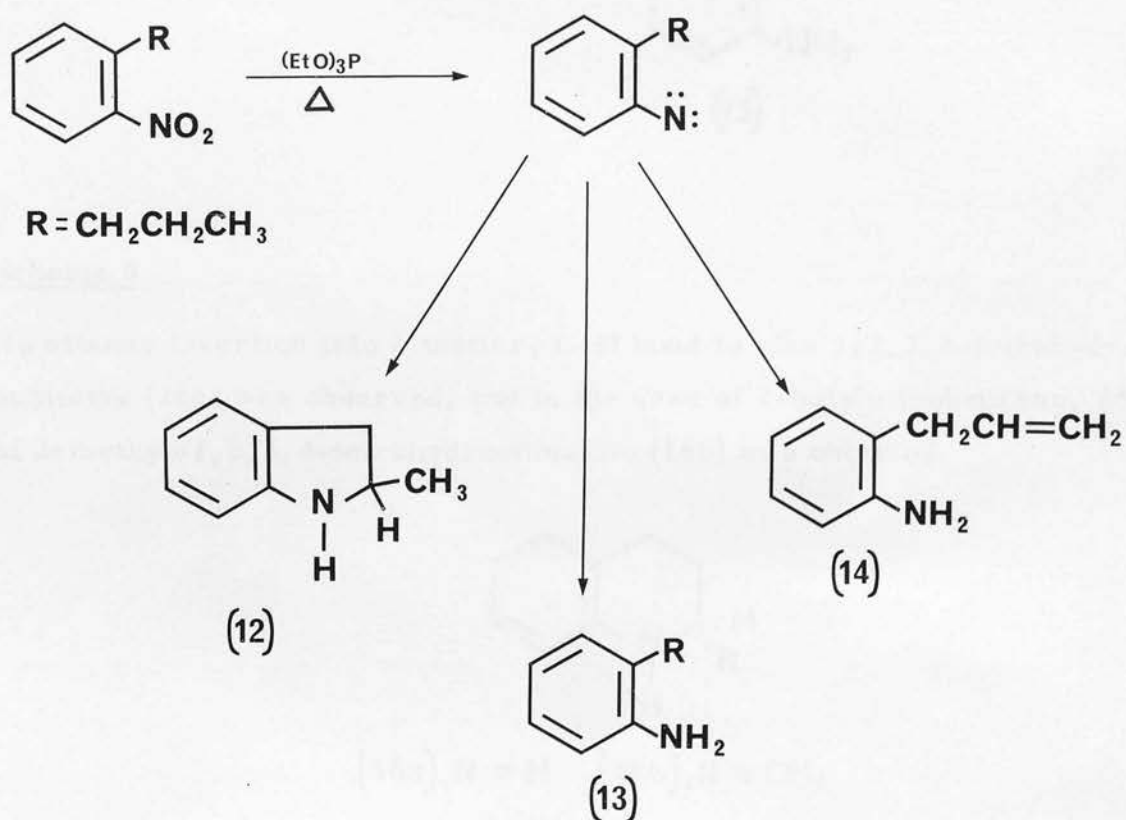


Scheme 5



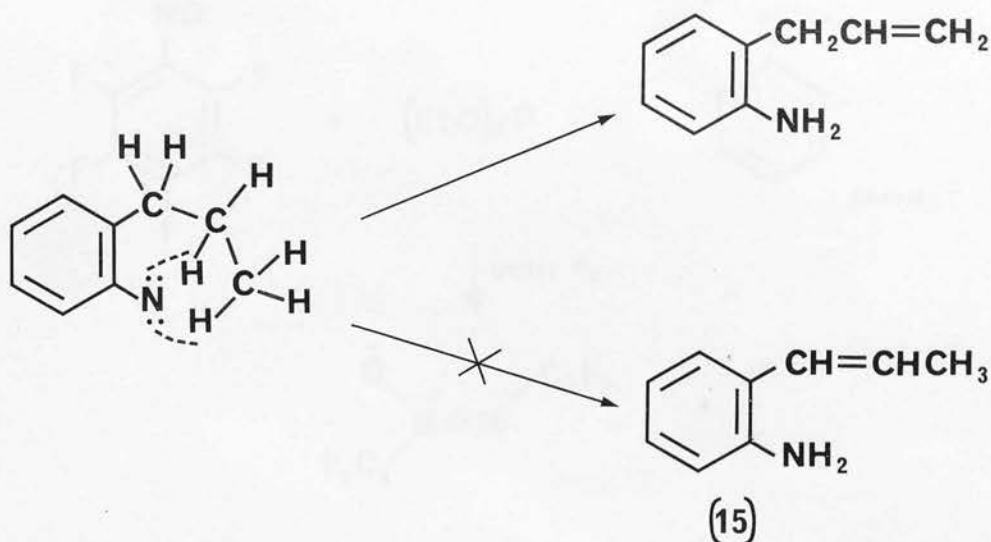
Scheme 6

(ii) Insertion Reactions. In the course of his studies of the phosphite deoxygenation of 2-alkylnitrobenzenes, Sundberg^{16c} observed that 2-propyl-, 2-butyl, and 2-cyclohexylnitrobenzene gave, in addition to the phosphorimides discussed above, under (i), small yields (6.5-14%) of indolines and ca 10% of products attributable to hydrogen abstraction by the nitrene. For example, 2-propylnitrobenzene gave 6.5% of 2-methylindoline (12), 2.7% of 2-propylaniline (13), and 6.0% of 2-(3-propenyl)aniline (14) (Scheme 7).



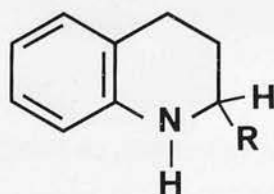
Scheme 7

Whether the indoline is formed by an abstraction-recombination process or by direct insertion of the nitrene into the C-H bond, is not discussed. However an explanation for the absence of 2-(1-propenyl)aniline (15) is given in terms of a concerted mechanism (Scheme 8).



Scheme 8

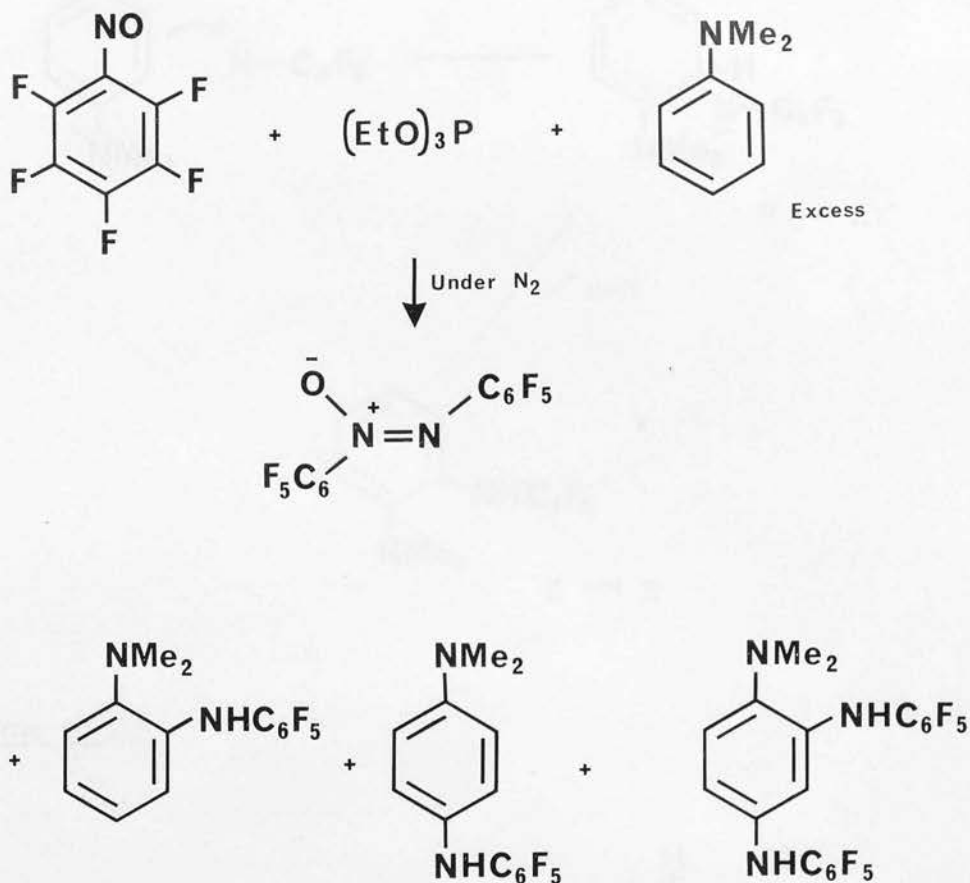
No nitrene insertion into a tertiary C-H bond to give 1,2,3,4-tetrahydroquinoline (16a) was observed, but in the case of 2-butyl nitrobenzene, 2% of 2-methyl-1,2,3,4-tetrahydroquinoline (16b) was obtained.



(16a), R = H (16b), R = CH₃

The absence of a product derived from nitrene insertion into a tertiary C-H bond has also been reported by Sadogan and his co-workers, who detected no indoline after the deoxygenation of 2-ethylnitrosobenzene,¹⁴ nor after the deoxygenation of 2-ethylnitrobenzene.^{17b} The latter result confirms a previous report by Sundberg.^{16a}

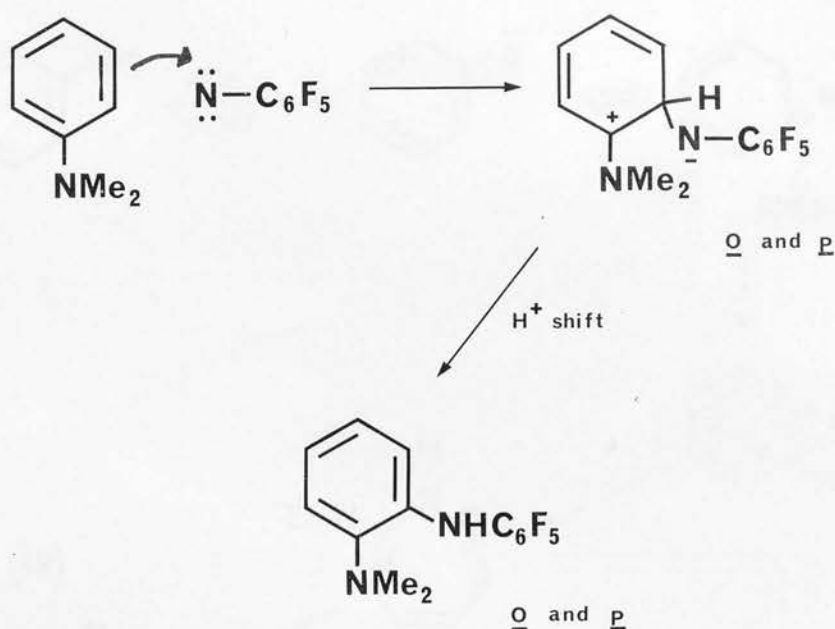
An intermolecular insertion reaction has been observed by Abramovitch and Challand¹⁹ who reacted pentafluoronitrosobenzene with triethyl phosphite in N,N-dimethyl aniline and obtained a total of 18% of substituted N,N-dimethylanilines (Scheme 9). In addition 1.1% of



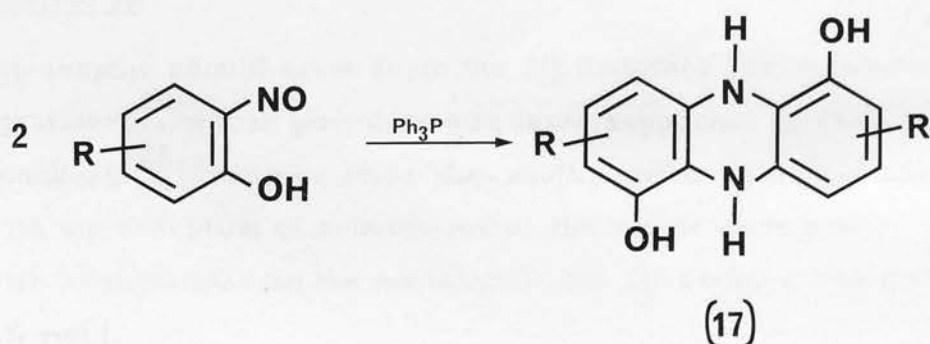
Scheme 9

decafluoroazoxybenzene was obtained, contrasting sharply with the 80% yield of the azoxy-compound reported by Burdon and his co-workers,²⁰ who used benzene as solvent. In view of the highly electrophilic nature of pentafluorophenylnitrene the formation of the N,N-diarylamines can be rationalised in terms of an electrophilic aromatic substitution of the solvent (Scheme 10).

Another example of a similar insertion has been reported by Charalambous and his co-workers²¹ who reported that deoxygenation of 2-nitrosophenols by triphenyl phosphine gave 1,6-dihydroxy-5,10-dihydro-phenazines (17) in ca. 50% yield (Scheme 11).



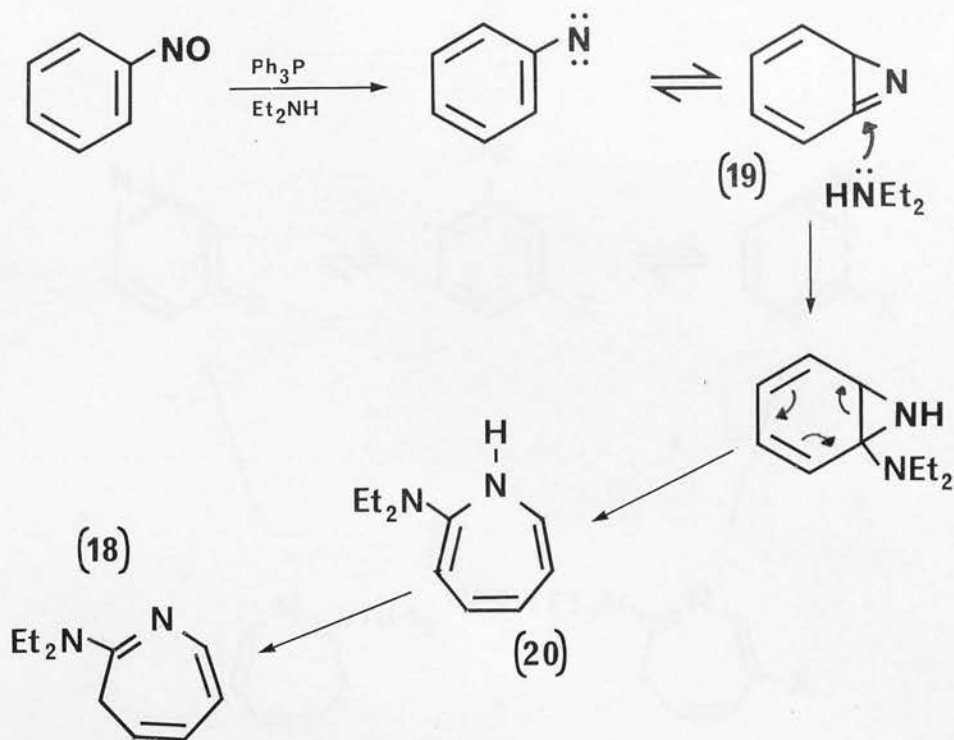
Scheme 10



Scheme 11

(iii) Ring Expansions. In 1966, Odum and Brenner²² showed that the reaction of nitrosobenzene with triphenyl or tri-*n*-butyl phosphine in the presence of a nucleophile, diethylamine, gave 2-diethylamino-3H-azepine (18) in 62% yield (Scheme 12).

The 7-azabicyclo[4, 2, 0]heptatriene (19) was first suggested by Huisgen and his co-workers²³ to explain the formation of 2-amino-3H-azepines during the thermolysis of phenyl azide in amines. That the

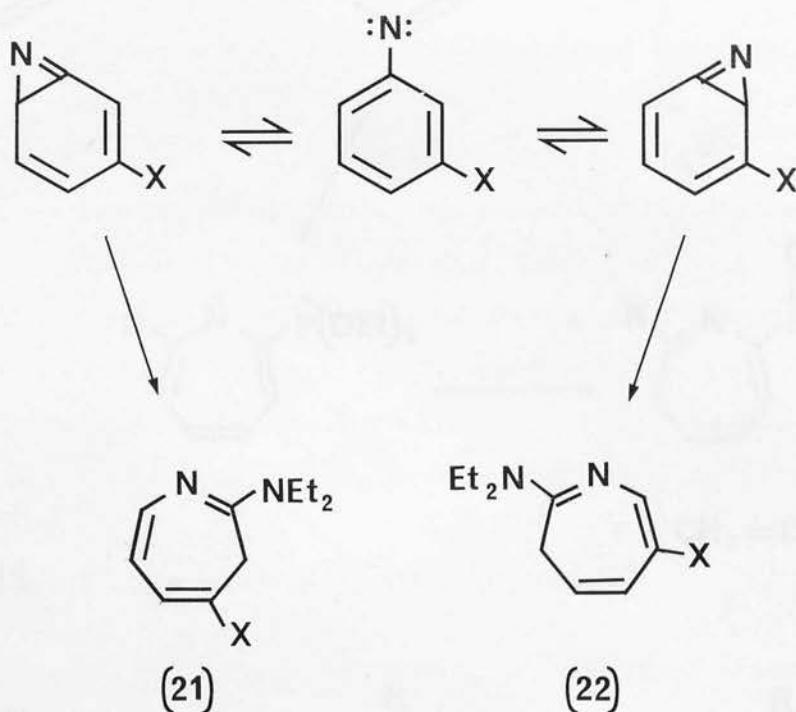


Scheme 12

3H-azepine should arise from the 1H tautomer (20) was first suggested by Maier,²⁴ whose postulate was later supported by results obtained by Sundberg.²⁵ Amines other than diethylamine also gave azepines,²² but with the exception of n-butylamine, the yields were lower; for example, with methylamine as the nucleophile the 3H-azepine was formed in only 4% yield.

There quickly followed reports²⁶ of an analogous reaction between nitrobenzene and the more reactive deoxygenating reagent,²⁶ diethylmethylphosphonite, $(\text{EtO})_2\text{PMe}$, which, in the presence of diethylamine, gave 2-diethylamino-3H-azepine in 83% yield. Atherton and Lambert²⁷ extended this reaction with amines by using substituted nitrobenzenes and tris-(dialkylamino)phosphines, and Cadogan and his co-workers²⁸ deoxygenated a range of substituted nitrobenzenes with diethylmethylphosphonite and diphenylethylphosphinite, Ph_2POEt . In most cases good yields of the corresponding 3H-azepines were obtained, and both teams of workers noted that meta-substituted nitrobenzenes gave a mixture of the 4- and 6-substituted 3H-azepines, (21) and (22). This is substantial evidence in support of the

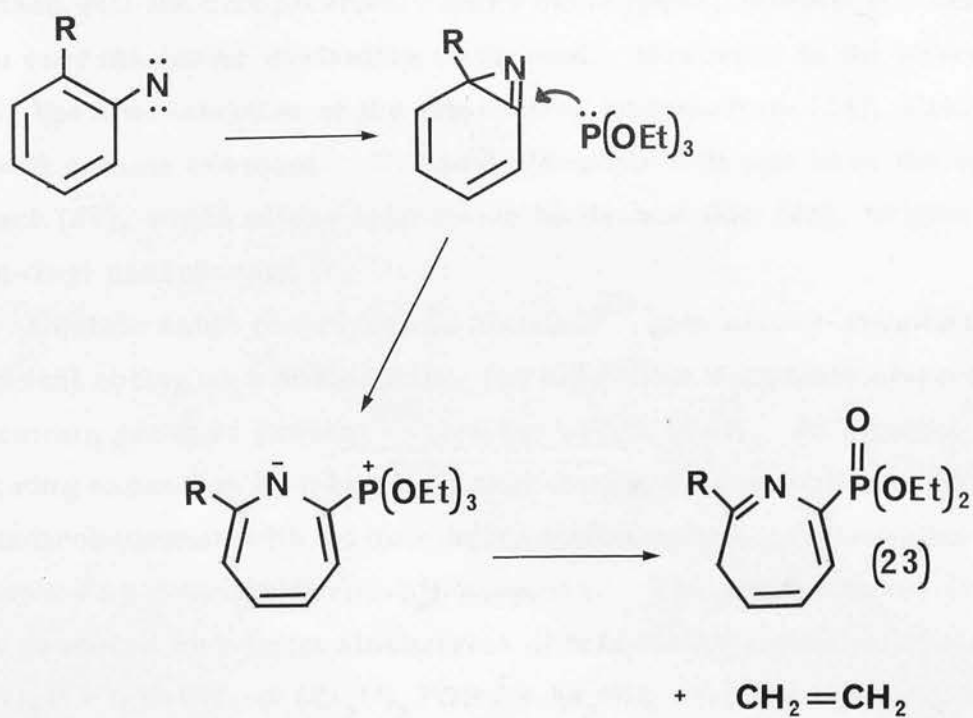
postulated mechanism (Scheme 13), in which the nitrene may ring-close



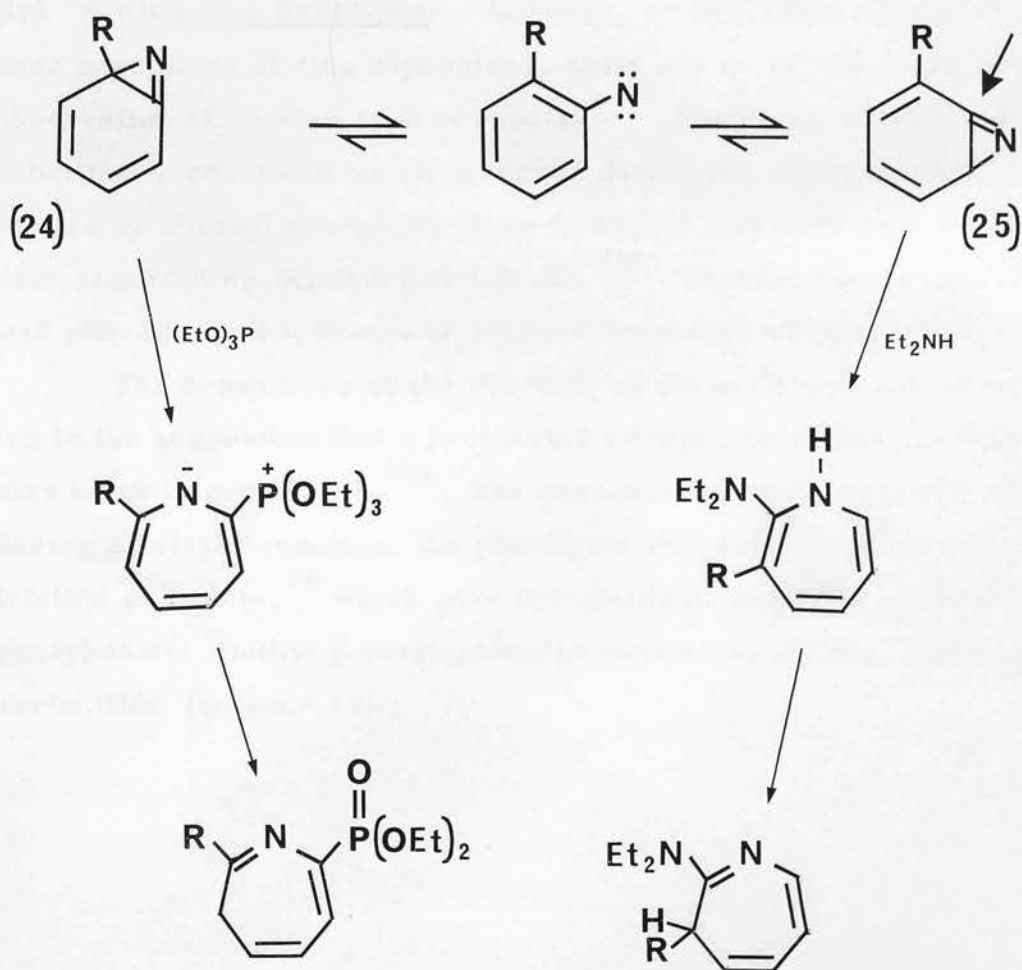
Scheme 13

in both possible directions to give two different intermediates, and hence the mixture of (21) and (22).

Nucleophiles other than amines can also promote ring-expansion of aryl nitrenes,^{17, 18, 29} but the yields of azepines are very poor compared to those obtained in the presence of diethylamine. In deoxygenations of 2-alkylnitrobenzenes by triethyl phosphite,^{17, 18} the phosphorus reagent itself can act as a nucleophile and small yields (less than 18%) of the corresponding 3H-azepin-7-yl-phosphonates (23) are obtained (Scheme 14). The position of substitution of the phosphonate group is in marked contrast to that observed for the diethylamino-group,²⁶ and to account for this Cadogan and his co-workers²⁸ have suggested the following (Scheme 15). Two possible azabicyclic intermediates, (24) and (25), are in equilibrium with the aryl nitrene, but (25) will be present in much higher concentration for steric reasons. A small nucleophile such as Et_2NH will have easier access to the point of attack (arrowed) of this predominant species



Scheme 14



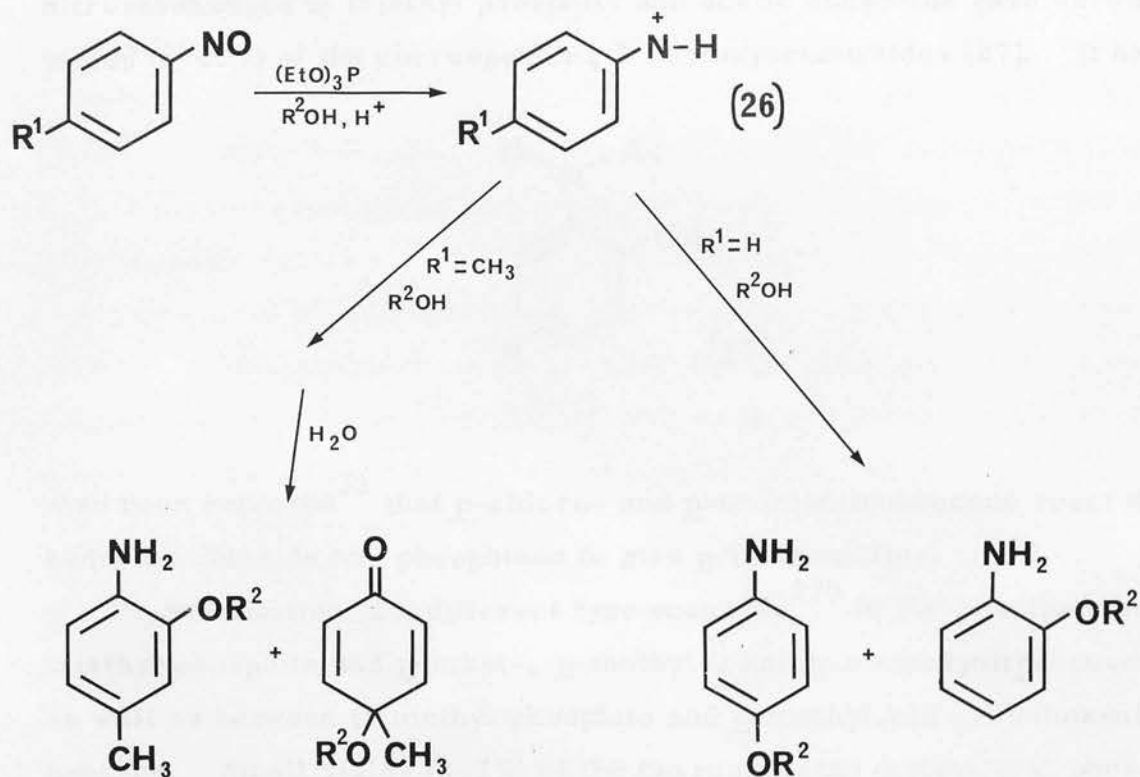
Scheme 15

(25), than will the comparatively bulky nucleophile, triethyl phosphite, and so only the amine derivative is formed. However, in the absence of amine, the concentration of the alternative intermediate (24), although low, will remain constant. Triethyl phosphite will now have the opportunity to attack (24), which offers less steric hindrance than (25), to give a 3H-azepin-7-yl phosphonate.

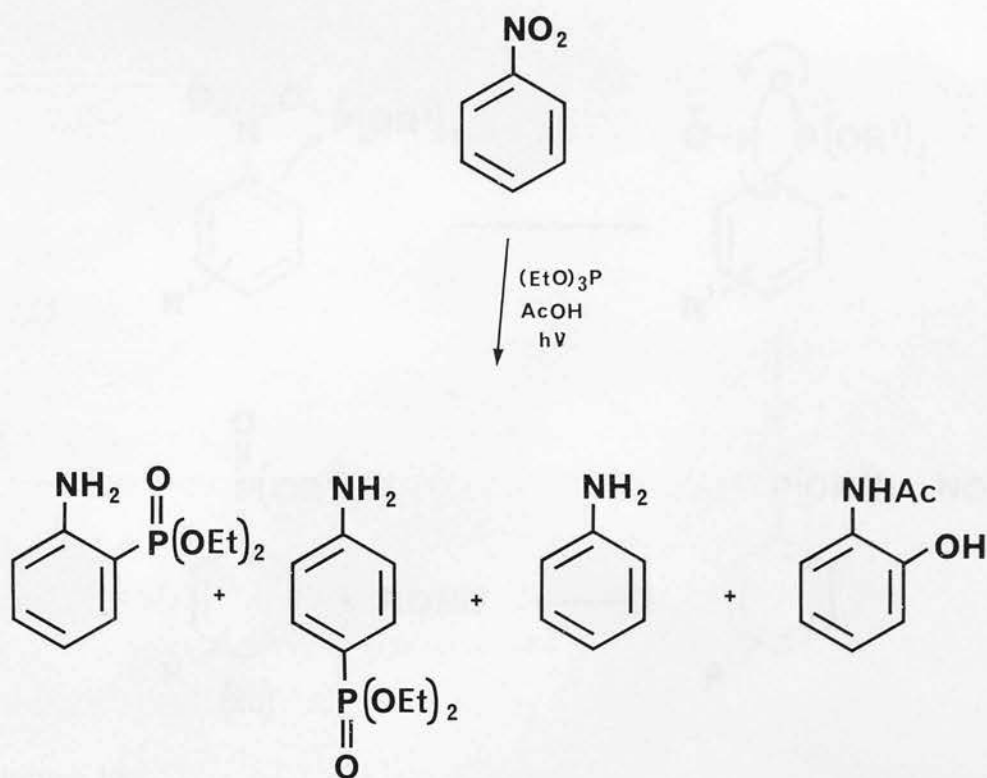
Certain azide photolyses in alcohols²⁹ give alkoxy-azepines, with the solvent acting as a nucleophile, but only when a suitable electron-withdrawing group is present^{29b} are the yields good. An attempt²⁸ to effect ring expansion by t-butyl alcohol during deoxygenation of *m*- and *p*-chloronitrobenzenes with tris(diethylamino)phosphine gave only the corresponding 2-diethylamino-3H-azepines. The small amount of diethylamine produced by t-butyl alcoholysis of tris(diethylamino)phosphine $[(\text{Et}_2\text{N})_3\text{P} + \text{t-BuOH} \rightarrow (\text{Et}_2\text{N})_2\text{POBu}^t + \text{Et}_2\text{NH}, \text{ etc}]$ had been sufficient to preferentially trap the intermediate nitrene.

(iv) Substitution Reactions. Although, as described above, alcohols are poor promoters of ring expansions, their use as solvents has led to the observation of another type of reaction. Examples of nucleophilic substitution reactions which occurred during the deoxygenation of nitrosoarenes by triethyl phosphite, when methanol was used as solvent, have been reported by Sundberg and Smith.^{29a} Substitution by other alcohols was also obtained if traces of acid were present (Scheme 16).

The dependence of the reaction on the acidity of the solvent has led to the suggestion that a protonated nitrene, or nitrenium ion, (26), may be an intermediate.^{29a} The presence of acetic acid was important during a related reaction, the photolysis of a solution of nitrobenzene in triethyl phosphite,³⁰ which gave low yields of diethyl *o*-aminophenylphosphonate, diethyl *p*-aminophenylphosphonate, aniline, and *o*-hydroxyacetanilide (Scheme 17).

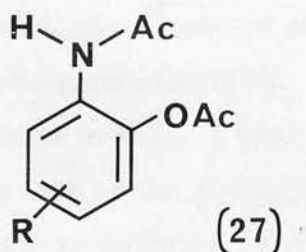


Scheme 16



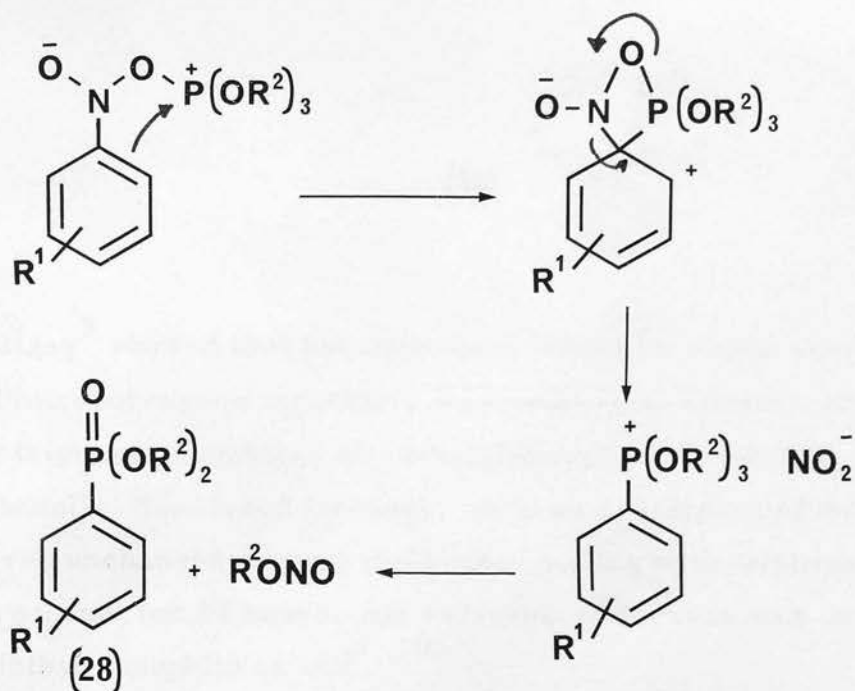
Scheme 17

At 0° , photolysis of solutions of nitrosobenzene and *o*- and *p*-methyl-nitrosobenzenes in triethyl phosphite and acetic anhydride gave varying yields (6-46%) of the corresponding 2-acetoxyacetanilides (27). It has



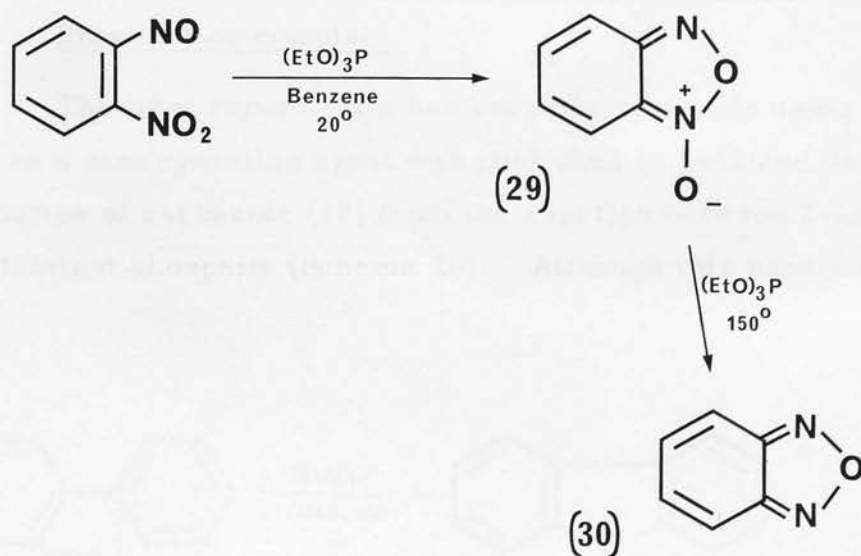
also been reported³¹ that *p*-chloro- and *p*-bromonitrobenzene react with hydrogen fluoride and phosphines to give *p*-fluoroaniline.

Substitution of a different type occurred^{17b} in the reactions between triethyl phosphite and *p*-ethyl-, *p*-methyl-, and *p*-methoxynitrobenzene, as well as between trimethyl phosphite and *p*-methyl and *o*-methoxynitrobenzene. Small yields (3-7%) of the corresponding dialkyl aryl phosphonates (28) were obtained, in which the nitro-group had been displaced by phosphite (Scheme 18).



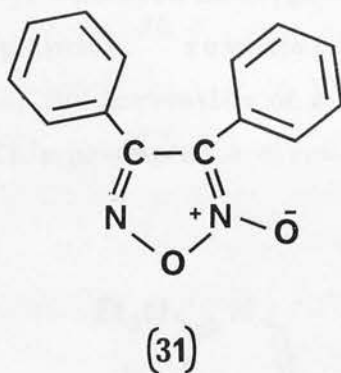
Scheme 18

o-Dinitroarenes, etc. The reaction of tervalent phosphorus compounds with ortho-di-functional benzenes has been examined. o-Dinitrobenzene undergoes reversible reaction with triethyl phosphine to give an unstable 1:1 adduct of undetermined structure.³² However, with triethyl phosphite as the reagent in boiling acetonitrile,³³ one of the nitro-groups is replaced to give diethyl o-nitrophenylphosphonate (75%). Reaction of o-dinitrobenzene with triphenyl phosphine in boiling benzene⁸ gives triphenyl phosphine oxide (48%) but the fate of the deoxygenated species is undetermined. o-Nitrosonitrobenzene is reduced by triethyl phosphite at room temperature in benzene³⁴ to give an 18% yield of benzofuroxan (29), which can be further reduced by triethyl phosphite at 150° to give benzofurazan (30), in 19% yield (Scheme 19).



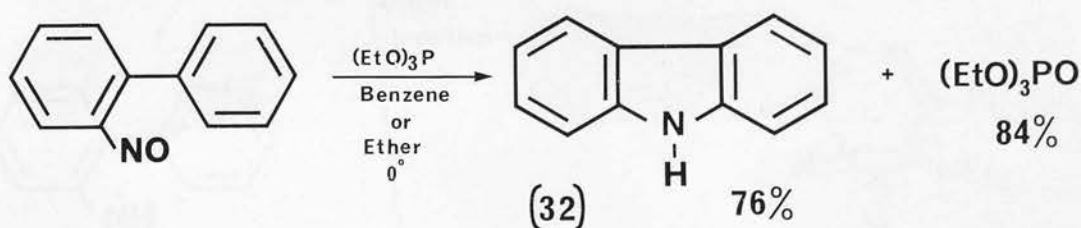
Scheme 19

Boyer and Ellzey⁸ showed that benzofuroxan, which they then thought to have the o-dinitrosobenzene structure, was reduced to benzofurazan in 68% yield by triphenylphosphine, tri-*n*-butylphosphine or triethyl phosphite in boiling ethanol. Non-fused furoxans, such as 3,4-diphenylfuroxan (31), were recovered unchanged in good yield after boiling with triphenyl phosphine in ethanol for 24 hours, but reduction to furazan was successful with pure triethyl phosphite at 160°. ^{10b}



A. 2 (b) Deoxygenation of 2-Nitro- and 2-Nitrosobiaryls, and Related Compounds.

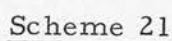
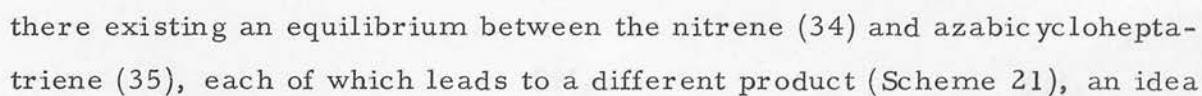
The first report² of a heterocyclic synthesis using phosphorus (III) as a deoxygenating agent was published in 1962 and described the formation of carbazole (32) from the reaction between 2-nitrosobiphenyl and triethyl phosphite (Scheme 20). Although this reaction was efficient



Scheme 20

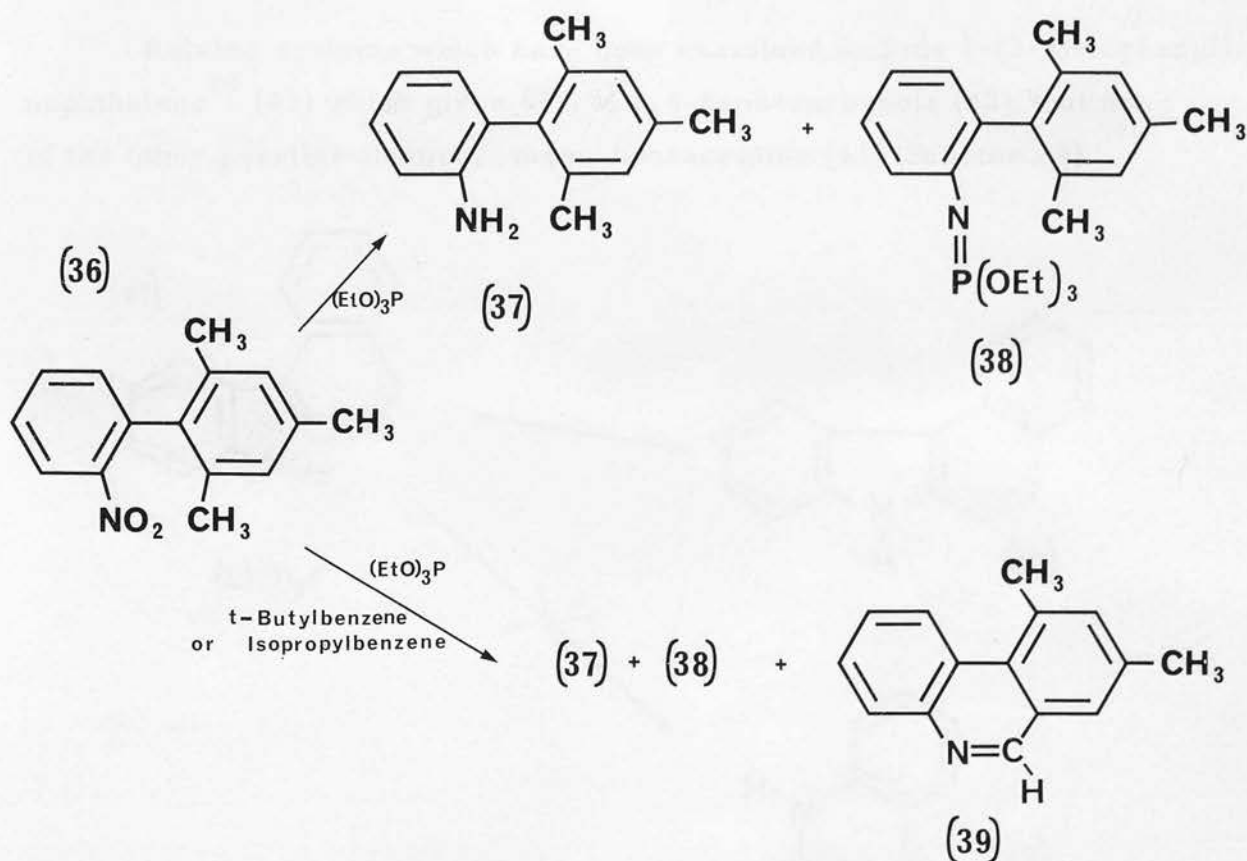
and simple to perform, its synthetic utility was severely limited by the difficulty in preparing analogous, substituted nitroso-compounds. The problem was soon overcome, however, when it was discovered¹ that 2-nitrobiphenyl also gave carbazole, in 83% yield, when treated with triethyl phosphite at 160°. The reaction was found to be quite general, and several carbazole derivatives have now been prepared from the

2-Nitrobiphenyl was also deoxygenated by diethyl methylphosphonite in an excess of diethylamine,²⁶ resulting in a decreased yield of carbazole (67%) and, in addition, the formation of 2-diethylamino-3H-3-phenylazepine (33) in 13% yield. This prompted a discussion^{26b} of the possibility of



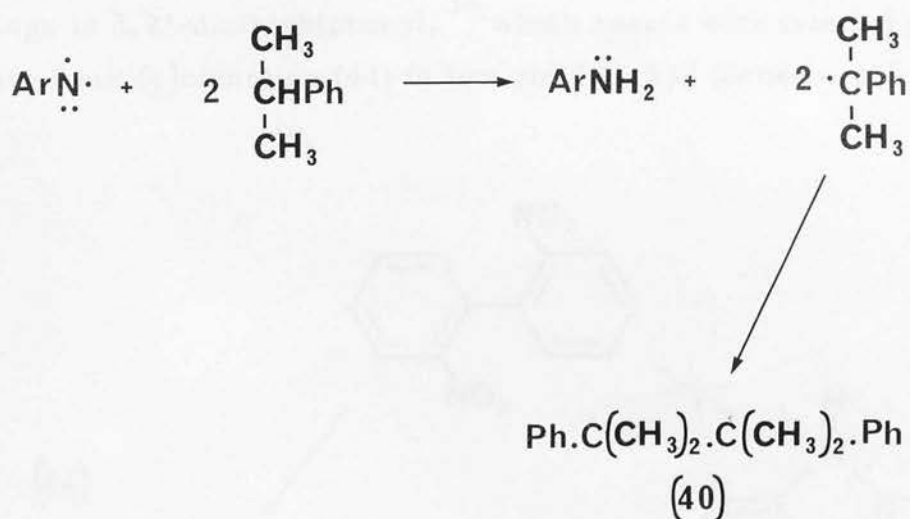
supported by Abramovitch and Davis.³⁶ The formation of carbazole from the nitrene may be via direct, concerted insertion [(i), scheme 21] or via an abstraction/recombination process [(ii), scheme 21].

When both ortho-positions of the ring subject to nitrene attack are blocked, as in the case of 2-nitro-2',4',6'-trimethylbiphenyl (36), no carbazole derivatives are formed.²⁶ When triethyl phosphite is the sole solvent, 2-amino-2',4',6'-trimethylbiphenyl (37), and the corresponding triethyl phosphorimidate (38) are obtained in 13% and 15% yields respectively. However, dilution in iso-propyl- or t-butylbenzene suppresses the coupling reaction sufficiently to allow the formation of 12 % of 8,10-dimethylphenanthridine (39) (Scheme 22).



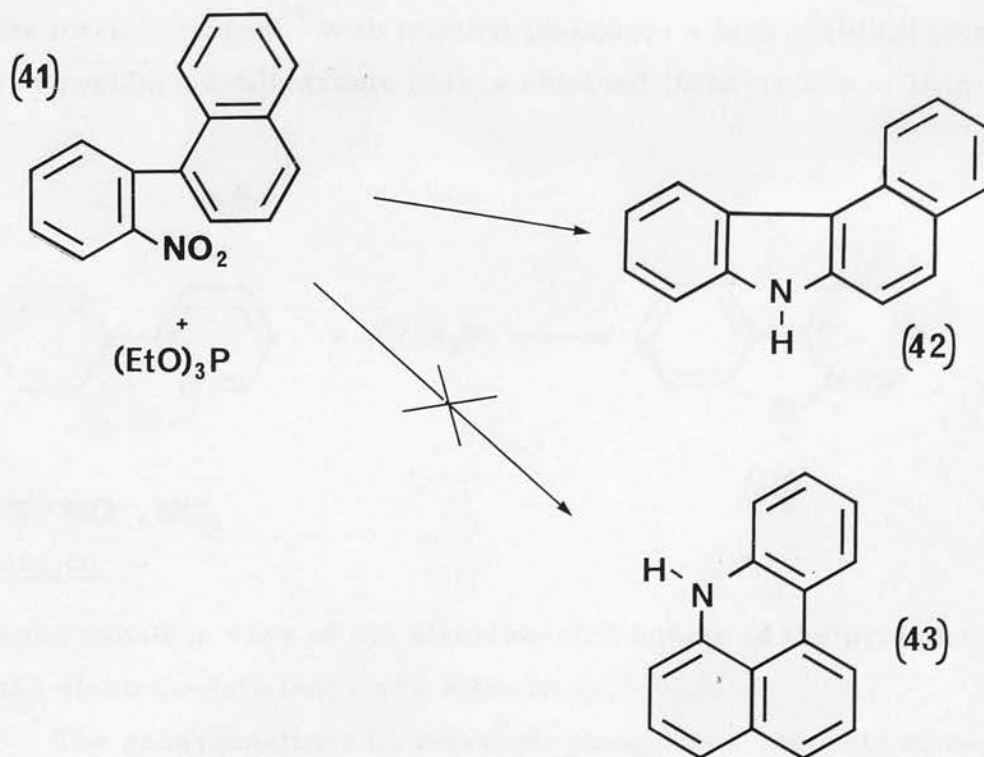
Scheme 22

In addition, when iso-propylbenzene is the solvent, 11% of bi- α -cumyl (40) is obtained, presumably by coupling of α -cumyl radicals formed when triplet nitrene abstracts a hydrogen atom from the iso-propylbenzene (Scheme 23).



Scheme 23

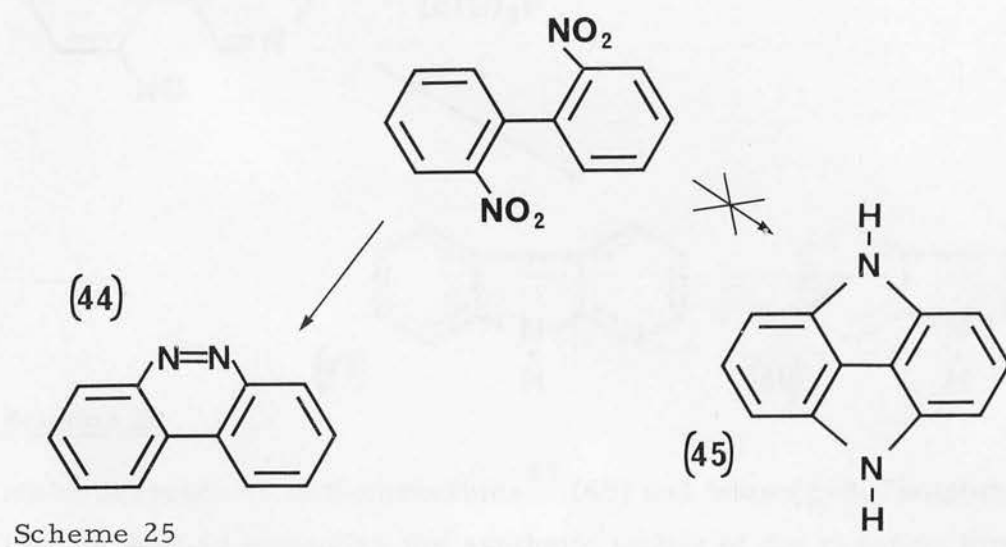
Related systems which have been examined include 1-(2-nitrophenyl)-naphthalene³⁴ (41) which gives 62% of 3,4-benzocarbazole (42), but none of the other possible isomer, meso-benzacridine (43) (Scheme 24).



Scheme 24

One example which does not follow the general trend to form five-membered

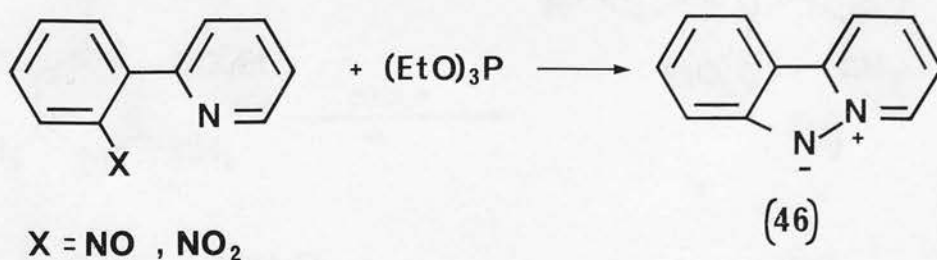
rings is 2,2'-dinitrobiphenyl,³⁴ which reacts with triethyl phosphite to give benzo[c]cinnoline (44) in low yield (1.5%) (Scheme 25). The alternative



Scheme 25

cyclisation product (45) is not obtained.

In the case of the deoxygenation of 2-(2-nitrosophenyl)pyridine¹⁴ and its nitro analogue³⁴ with triethyl phosphite a high yield (greater than 90%) of pyrido[1,2-*b*]indazole (46) is obtained (Scheme 26). This is the

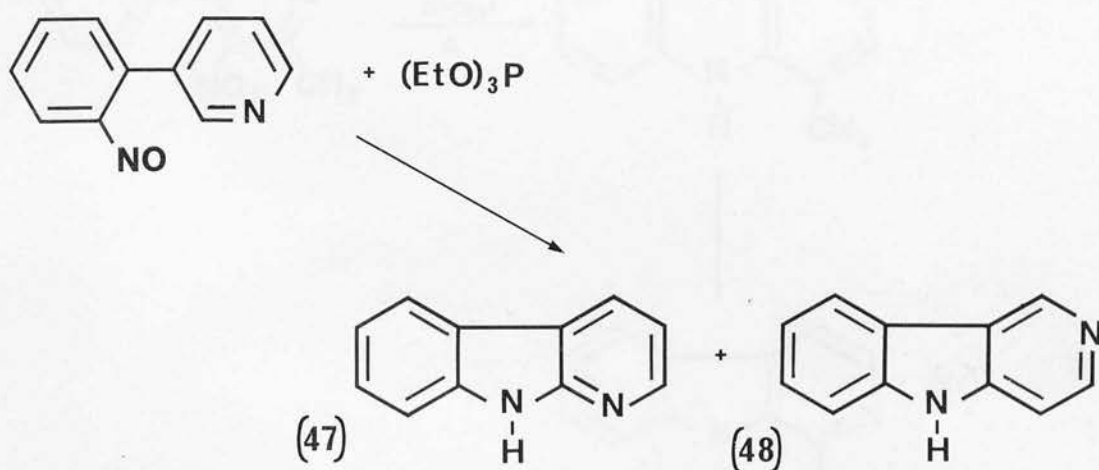


Scheme 26

expected result in view of the electron-rich nature of the pyridine nitrogen, and the electron-deficiency of a nitrene.

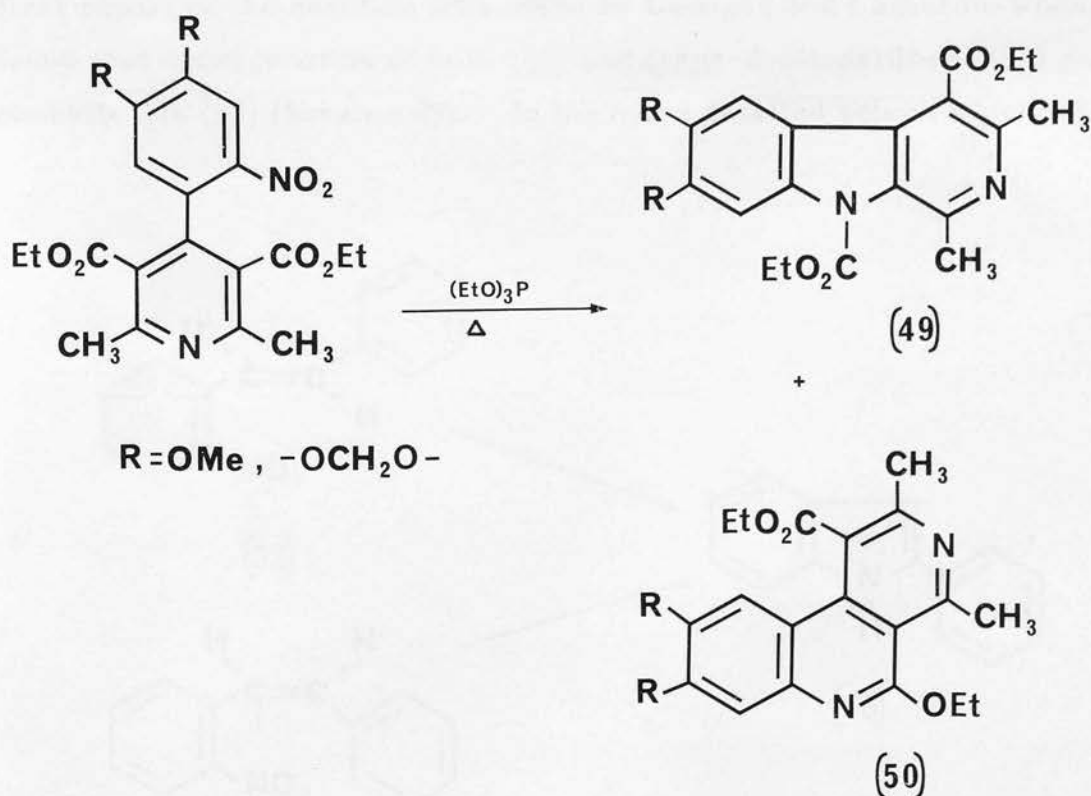
The deoxygenations by tervalent phosphorus reagents of several related compounds have also been studied; for example, reaction of 3-(2-nitrosophenyl)pyridine with triethyl phosphite gives a 64% yield of a mixture of α -carboline (47) (81.5%) and γ -carboline (48) (18.5%)

(Scheme 27). Kametani, and his co-workers have used the reaction to

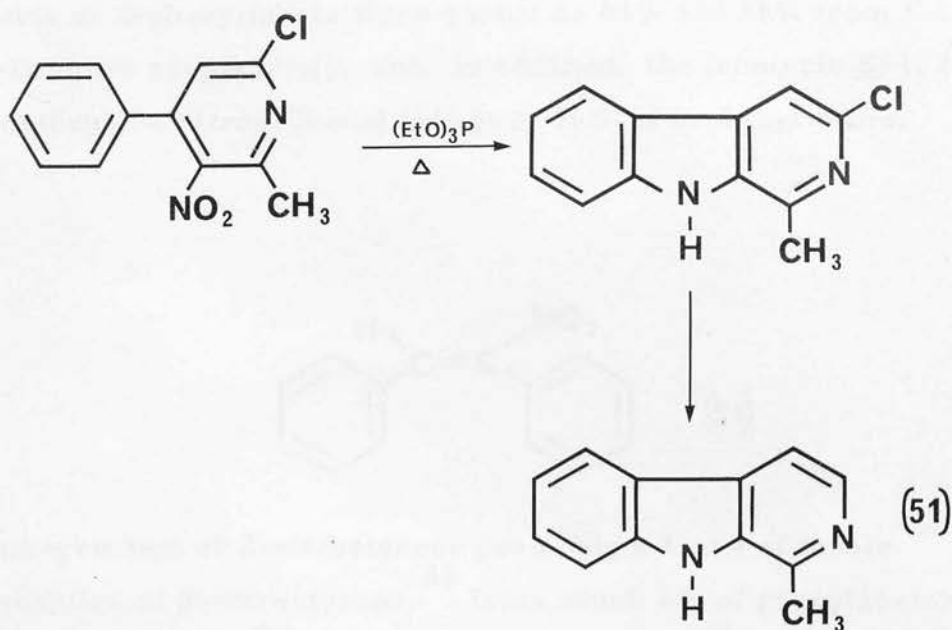


Scheme 27

make derivatives of β -carboline³⁷ (49) and benzo[*c*-2, 7]naphthyridines³⁷ (50) as well as extending the synthetic utility of the reaction into the natural-product field with the synthesis of the β -carboline alkaloid, harman³⁸ (51) (Scheme 28).



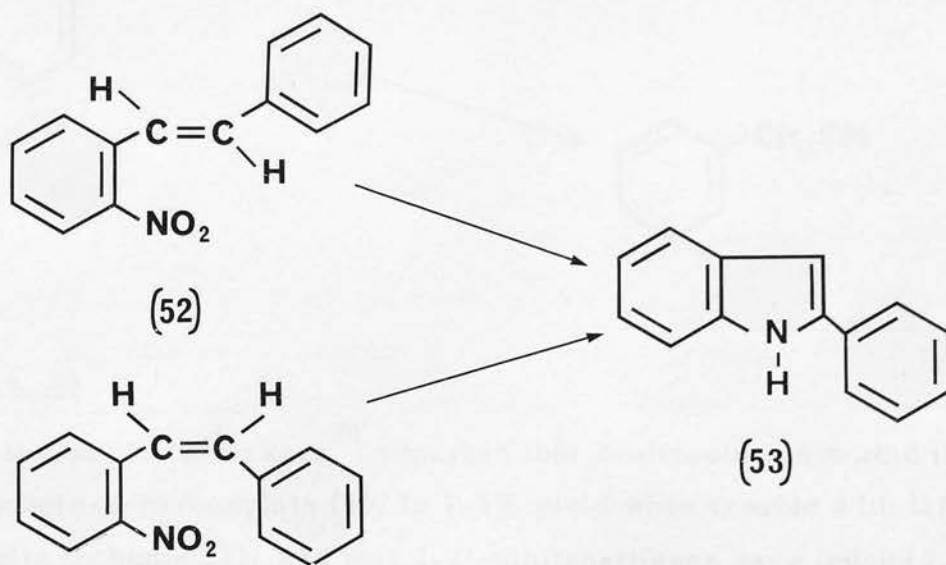
and,



Scheme 28

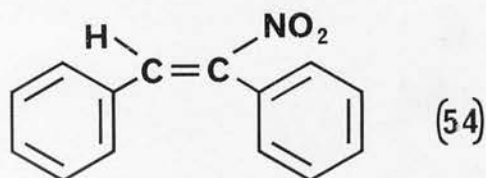
A. 2. (c) Deoxygenation of 2-Nitrostyrenes and Related Compounds

The reaction of substituted 2-nitrostyrenes with triethyl phosphite to form indoles has been examined closely by Sundberg,^{16a, 39, 40} but the first report of the reaction was made by Cadogan and Cameron-Wood,¹ who found that deoxygenation of both cis- and trans-2-nitrostilbene (52) gave 2-phenylindole (53) (Scheme 29). In the more detailed report which followed,³⁴

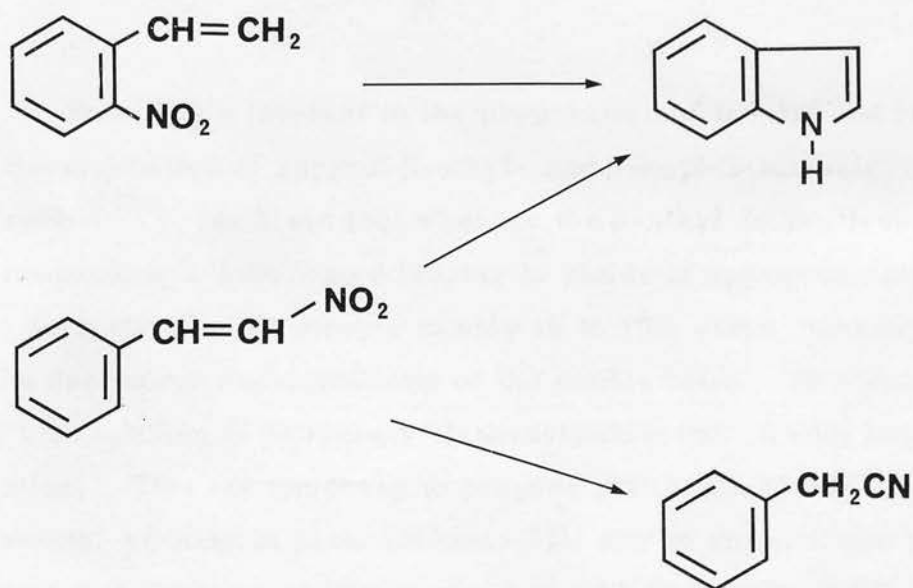


Scheme 29

the yields of 2-phenylindole were quoted as 85% and 58% from the cis- and trans-isomers respectively, and, in addition, the isomeric E-1, 2-diphenyl-1-nitroethene (α -nitrostilbene) (54) gave 16% of 2-phenylindole. However,

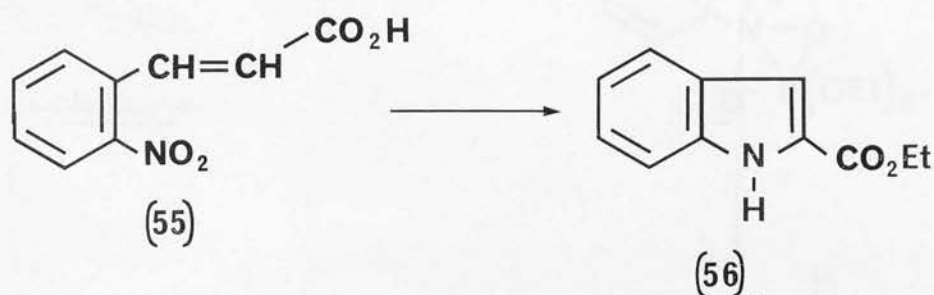


the deoxygenation of 2-nitrostyrene gave only a trace of indole,³⁴ as did deoxygenation of β -nitrostyrene,⁴¹ from which 6% of phenylacetonitrile could also be obtained⁴² (Scheme 30).

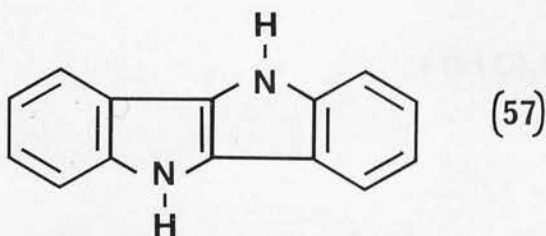


Scheme 30

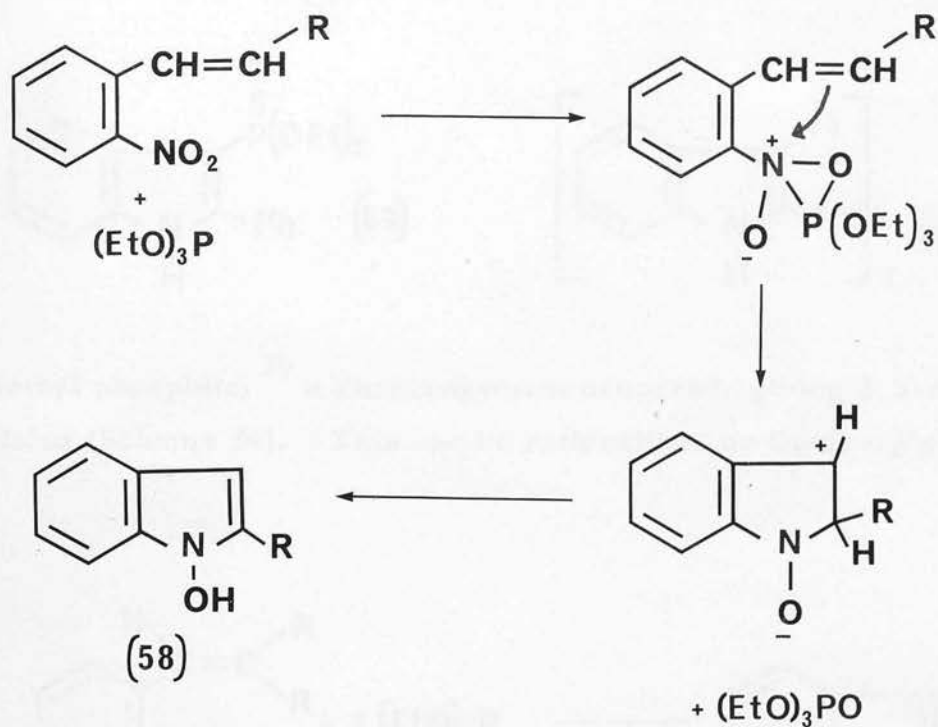
Cadogan and his coworkers³⁴ reported that 2-nitrocinnamic acid (55) gave ethyl indole-2-carboxylate (56) in 7.5% yield when treated with triethyl phosphite (Scheme 31), and that 2, 2'-dinitrostilbene gave indolo[3, 2-b]indole (57) in 2% yield.



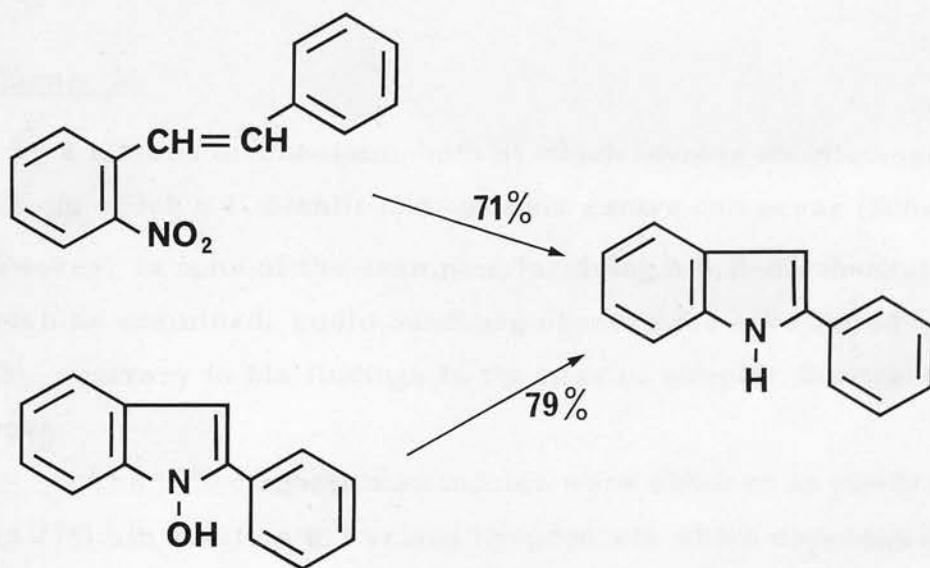
Scheme 31



Sundberg's interest in the preparation of indoles led him to investigate the deoxygenation of several β -alkyl- and β -acyl-2-nitrostyrenes by triethyl phosphite.^{16a} He found that whereas the β -alkyl derivatives gave the corresponding 2-substituted indoles in yields of approximately 50%, the β -acyl derivatives gave indoles in only 16 to 19% yield, possibly as a result of the decreased nucleophilicity of the double bond. Of mechanistic significance was the isolation of 1-hydroxy-2-phenylindole (58; $\text{R}=\text{Ph}$) from an interrupted reaction. This led Sundberg to propose that a non-nitrene pathway was operating, at least in part, (Scheme 32), and to support this postulate, he showed that reaction of 1-hydroxy-2-phenylindole (58; $\text{R}=\text{Ph}$) with triethyl phosphite gave the same products (2-phenylindole and small yields of by-products) as were obtained from the completed deoxygenation of trans-2-nitrostilbene (Scheme 33). The by-products from both of these reactions were



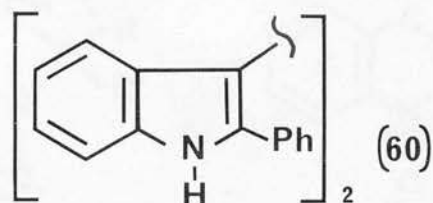
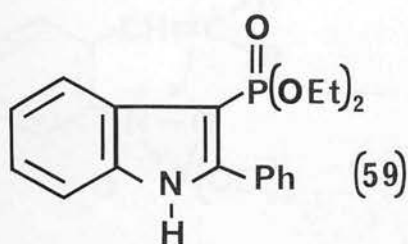
Scheme 32



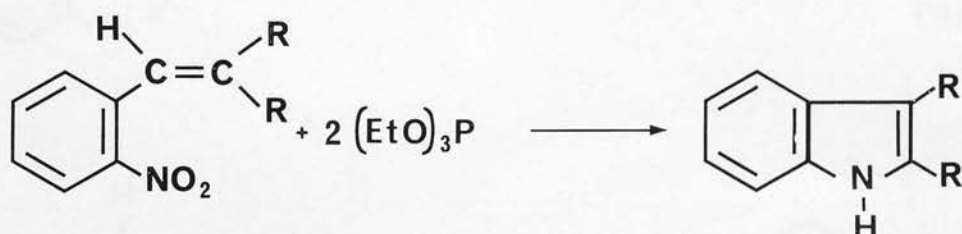
Scheme 33

diethyl 2-phenyl-3-indolylphosphonate (59; 2-9%) and 2, 2'-diphenyl-3, 3'-bi-indolyl (60; 7-11%), but the mechanism of their formation is unclear.

When β, β -disubstituted-2-nitrostyrenes were deoxygenated with



triethyl phosphite,³⁹ a rearrangement occurred, giving 2,3-disubstituted indoles (Scheme 34). This can be rationalised by Sundberg's mechanism

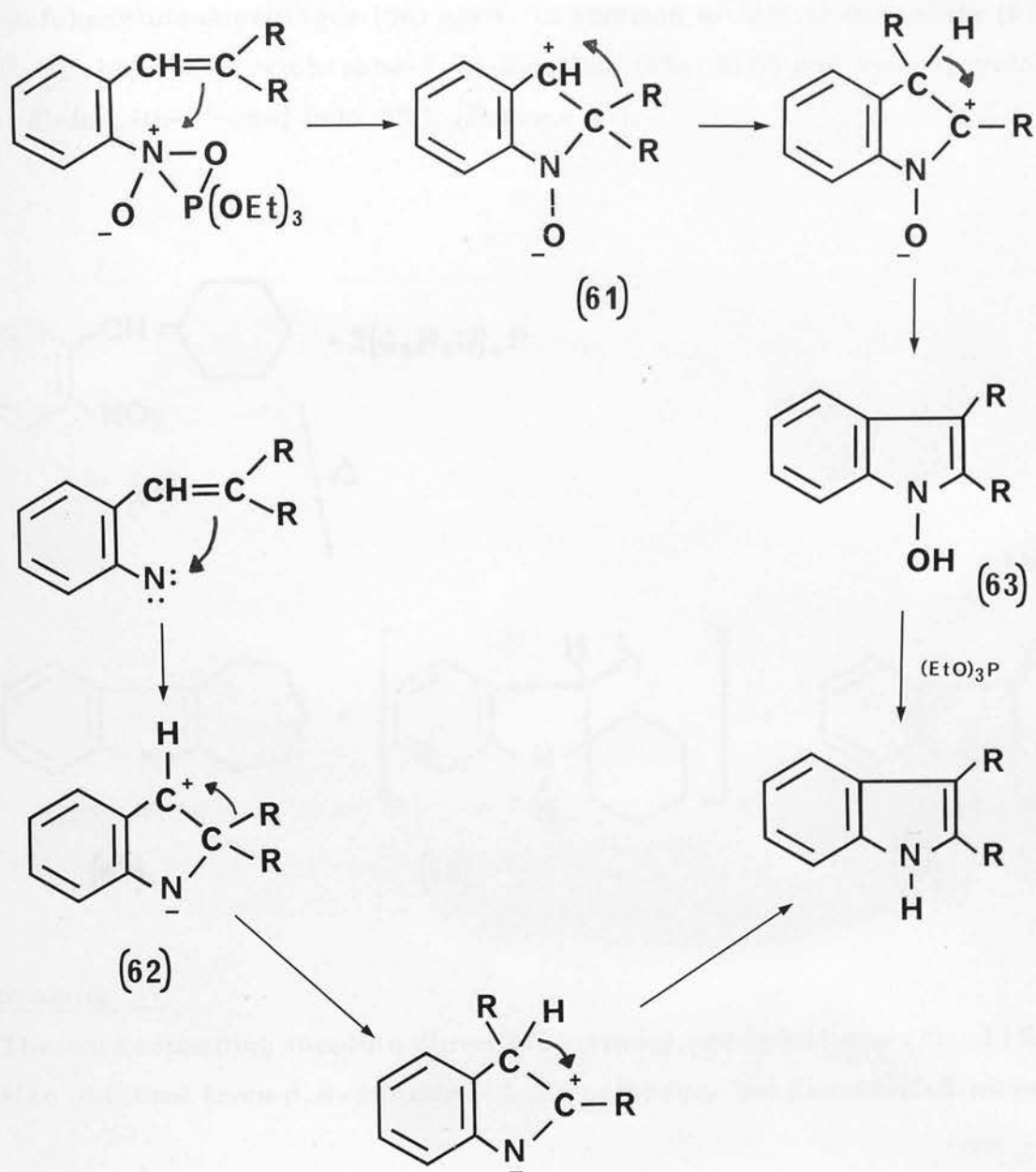


Scheme 34

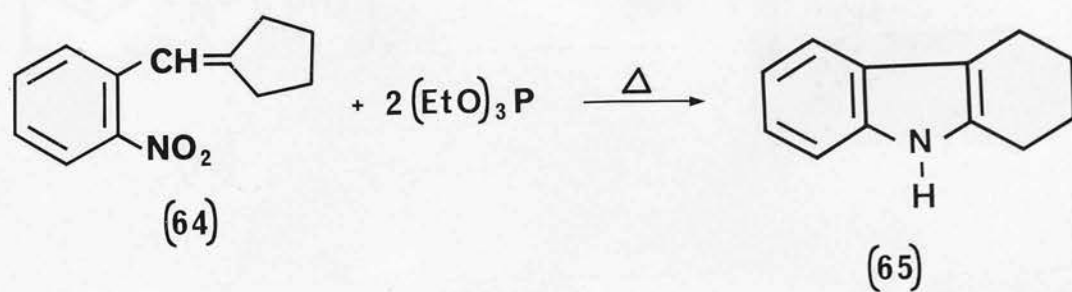
or by a nitrene mechanism, both of which involve an intermediate, (61) or (62), in which a 1,2-shift to a cationic centre can occur (Scheme 35).

However, in none of the examples involving a β,β -disubstituted-2-nitrostyrene which he examined, could Sundberg observe the substituted 1-hydroxyindole (63), contrary to his findings in the case of simpler 2-nitrostyrenes described above.

The 2,3-disubstituted indoles were obtained in yields of between 15 and 77%, in addition to various by-products which depended on the substituents. Cyclopentylidene (*o*-nitrophenyl) methane (64) gave 1,2,3,4-tetrahydrocarbazole (65; 15%) as the only identified product (Scheme 36), but the

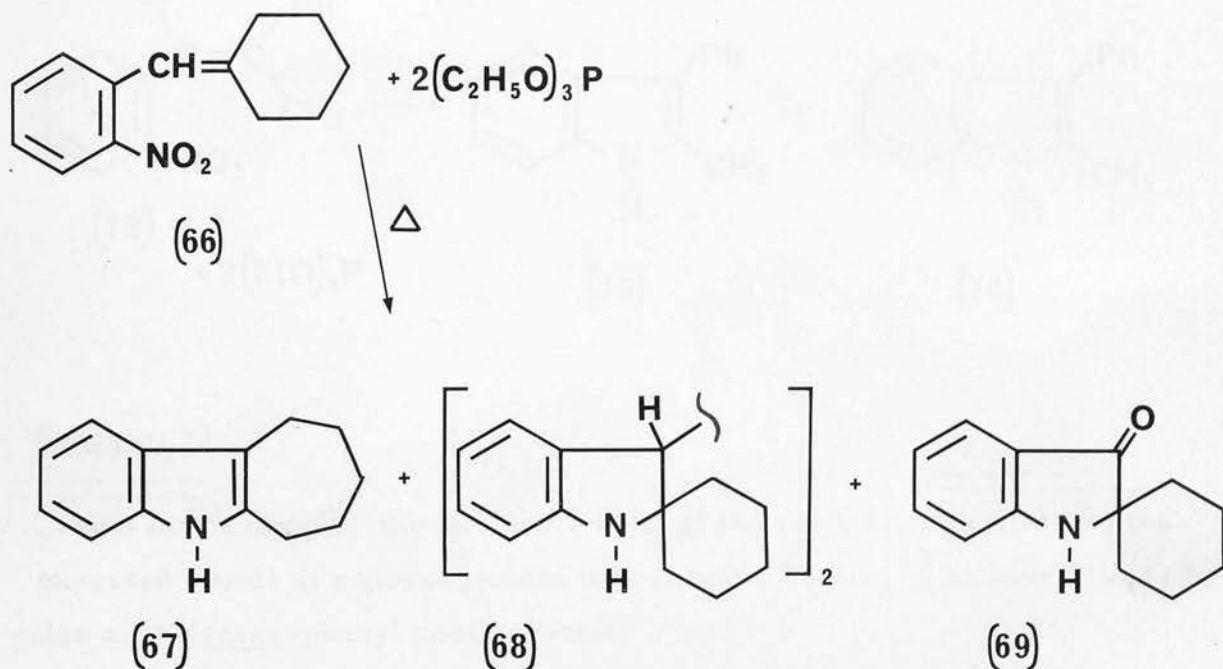


Scheme 35



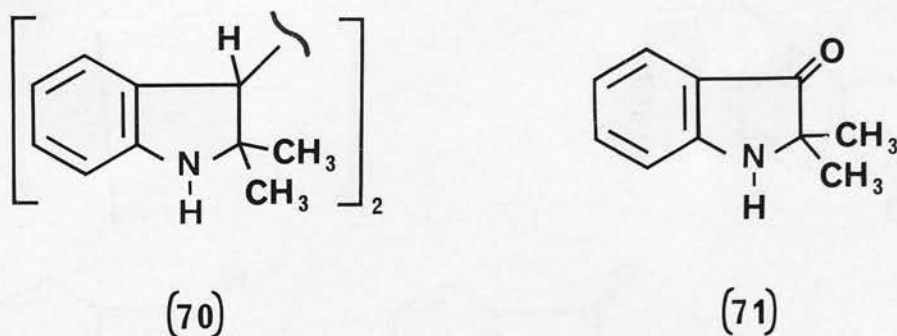
Scheme 36

cyclohexylidene analogue (66) gave, in addition to 35% of the indole (67), 3', 3'''-bispiro-[cyclohexane-1, 2'-indoline] (68; 24%) and spiro-[cyclohexane-1, 2'-indolin-3'-one] (69; 8%) (Scheme 37).

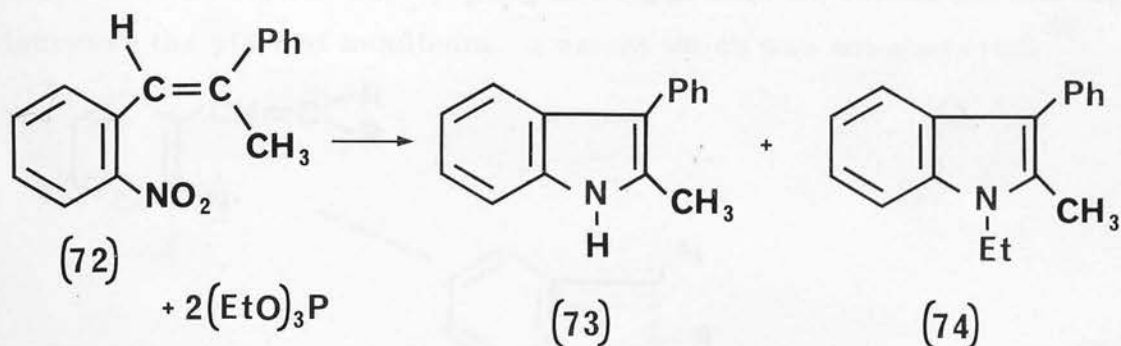


Scheme 37

The corresponding indoline dimer (70; trace) and indolinone (71; 11%) were also obtained from β, β -dimethyl-2-nitrostyrene, but β -methyl-2-nitro-trans-



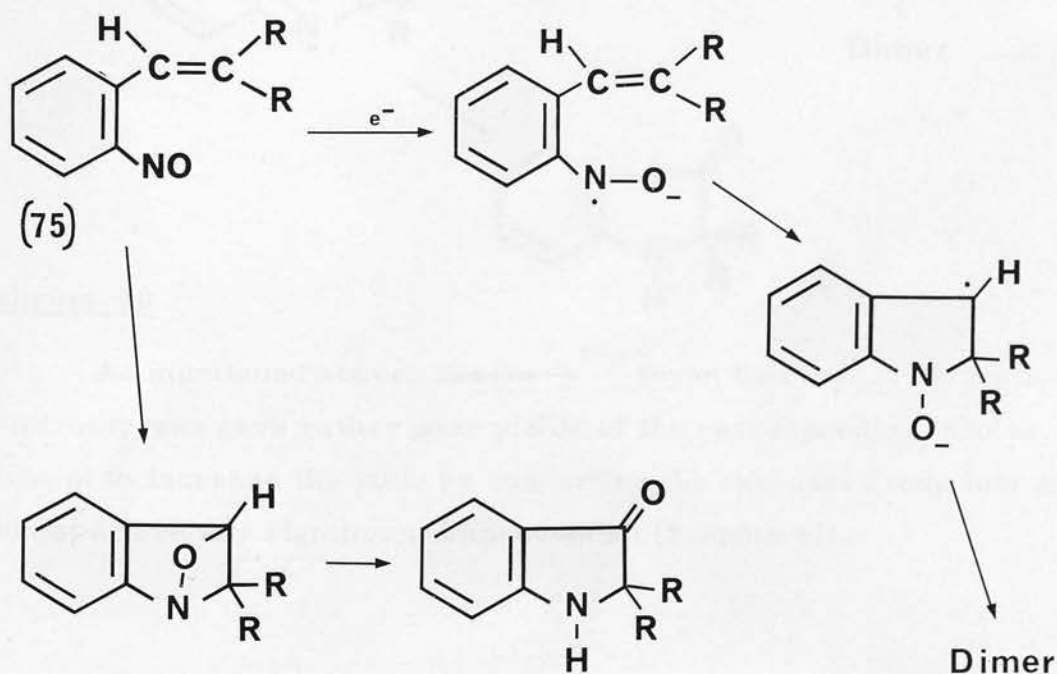
stilbene (72) gave only the indole (73; 7%) and *N*-ethyl-indole (74; 21%), presumably via ethylation of (73) by triethyl phosphate (Scheme 38).



Scheme 38

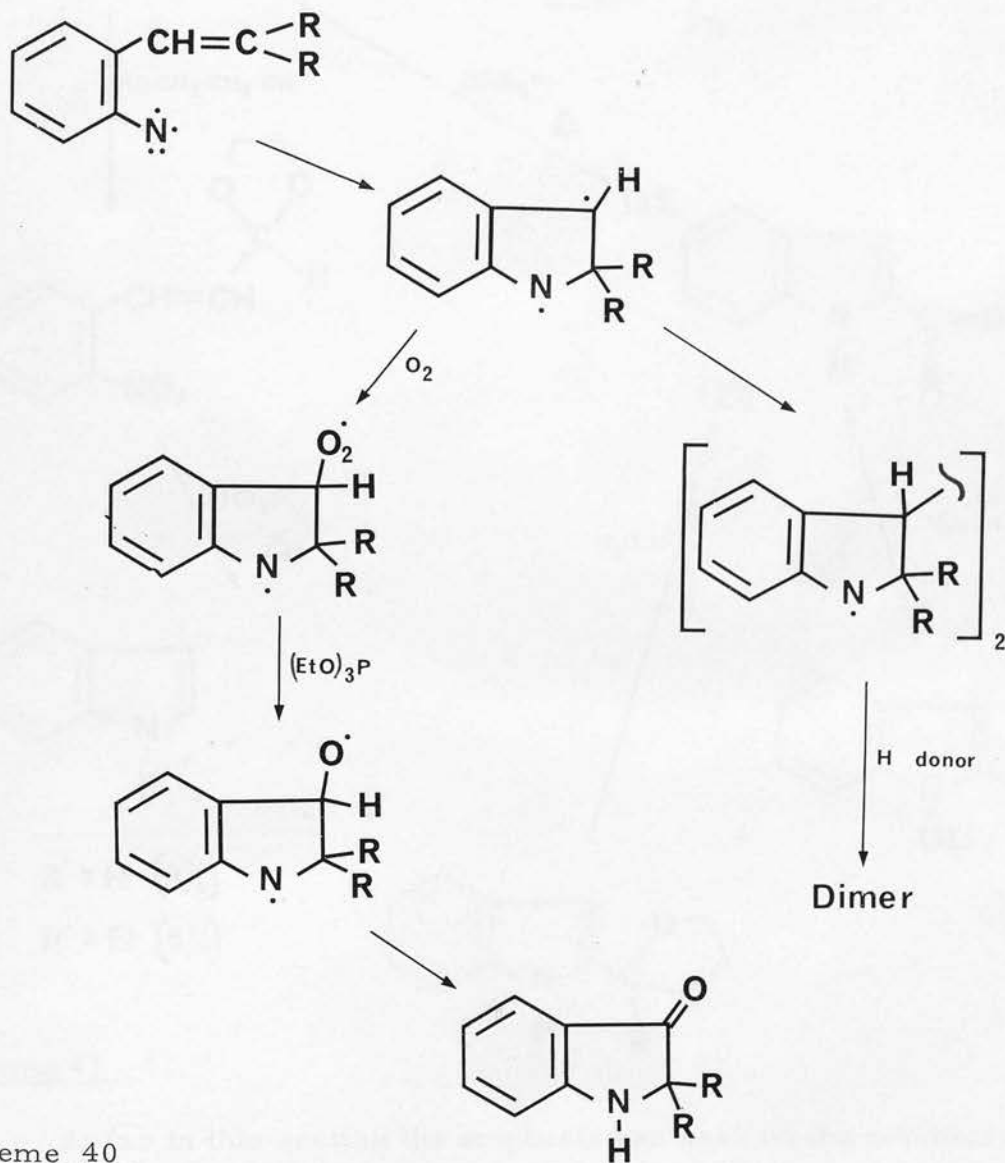
In this last example, the exclusive shift of the phenyl group could be the expected result of rearrangement to a cationic centre,⁴³ or may simply be due to the trans-phenyl configuration.

The formation of the bi-indolinyls and indolinones poses a difficult mechanistic problem. Sundberg³⁹ suggested that both products might arise from an intermediate nitrosostyrene (75) (Scheme 39), but, under the conditions of the reaction, such a nitroso-compound would be expected to



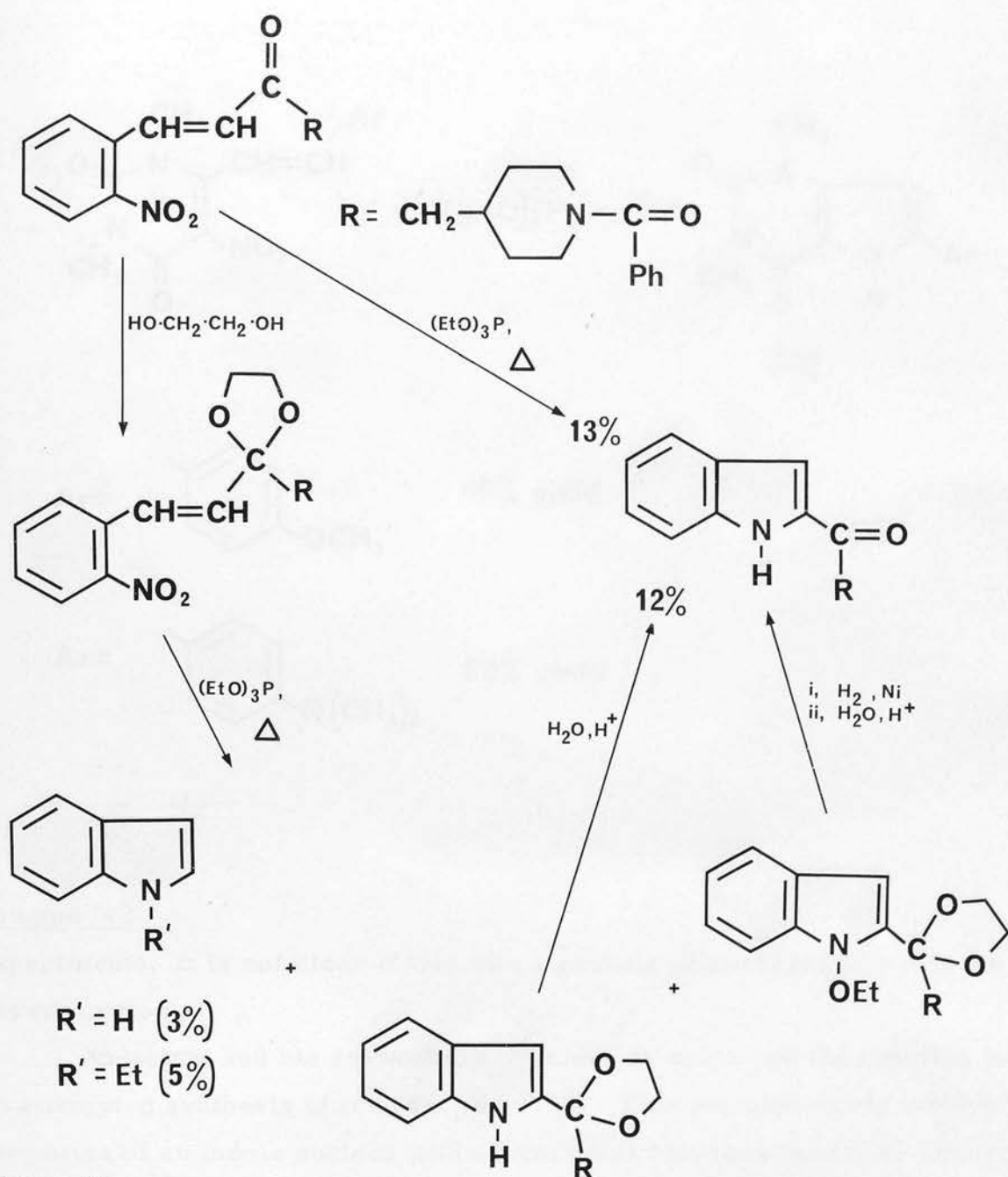
Scheme 39

undergo extremely rapid deoxygenation, rather than follow the suggested pathways. Cadogan³ proposed a mechanism involving a triplet nitrene (Scheme 40), which would cyclise to give a diradical as shown, but this suggests that increasing the concentration of oxygen in solution should increase the incidence of coupling of oxygen with the diradical, and hence increase the yield of indolinone, a result which was not observed.³⁹



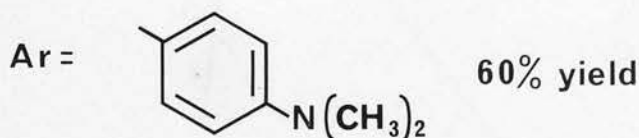
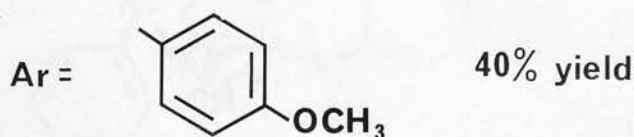
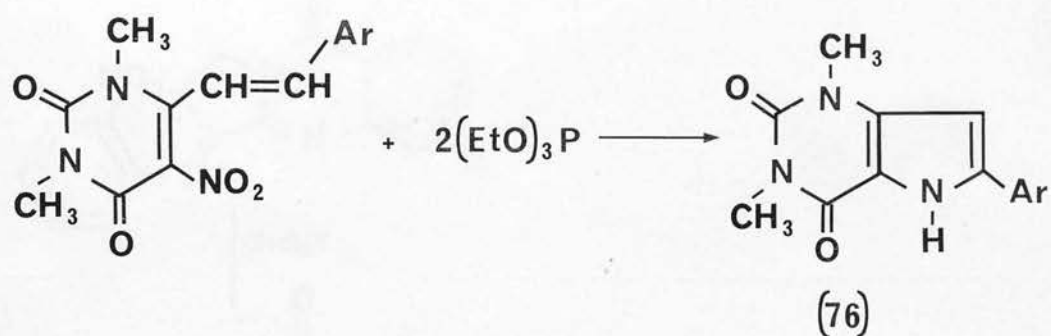
Scheme 40

As mentioned above, Sundberg^{16a} found that β -acyl derivatives of 2-nitrostyrene gave rather poor yields of the corresponding indoles, and an attempt to increase the yield by converting the carbonyl group into an acetal⁴⁰ did not afford any significant improvement (Scheme 41).



Scheme 41

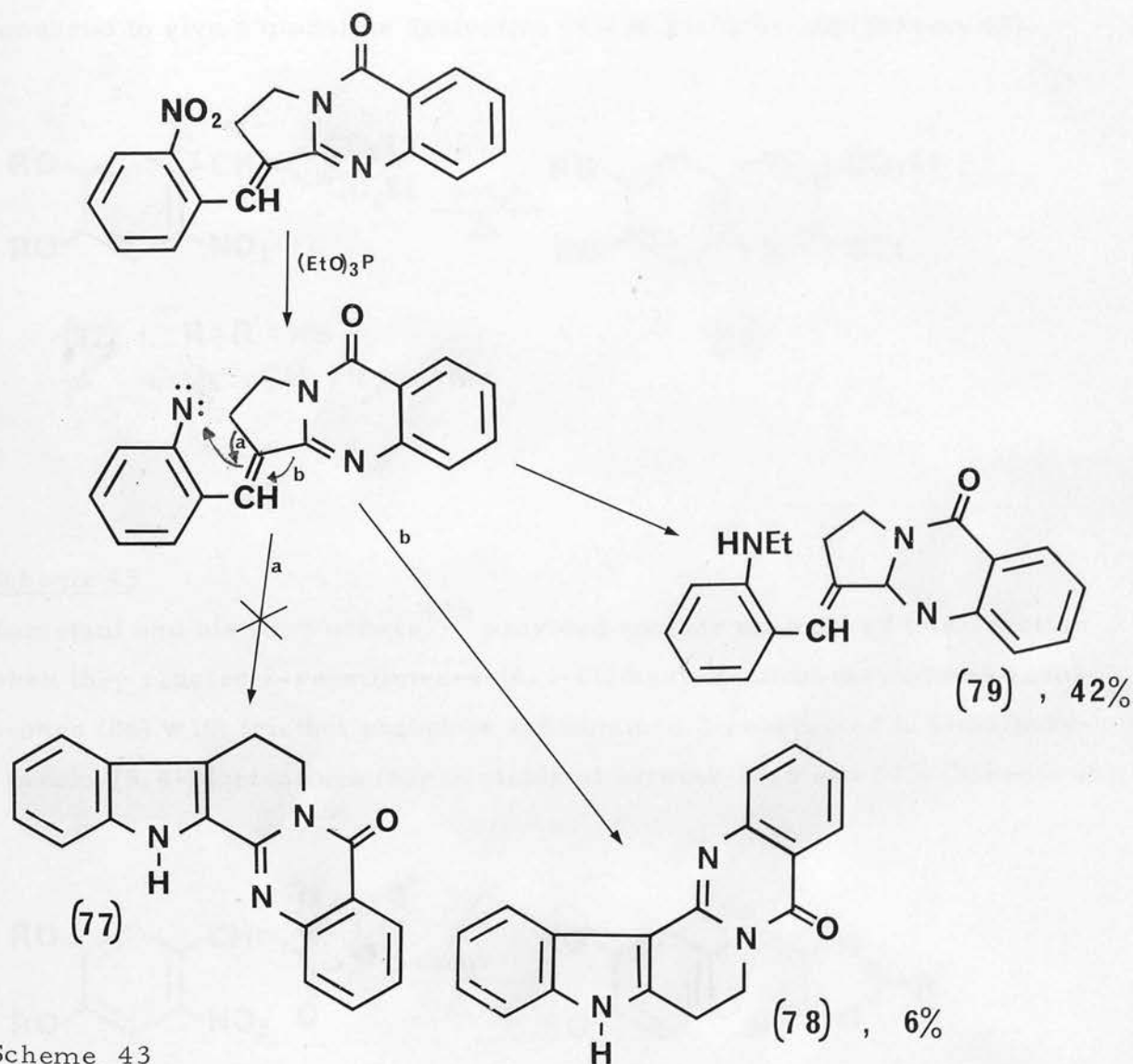
So far in this section the emphasis has been on the mechanism of the reaction, but several groups of workers, notably Kametani and his co-workers,⁴⁴ have employed the reaction to synthesise more complex heterocyclic systems. One of the first reports of this kind, was that of Taylor and Garcia,⁴⁵ who successfully prepared two pyrrolo[3, 2-d]pyrimidines (76) by reaction of the corresponding 5-nitro-6-styrylpyrimidine derivatives with triethyl phosphite, (Scheme 42). The reaction was induced both by heat and by photolysis, but since some heating occurred during the photolysis



Scheme 42

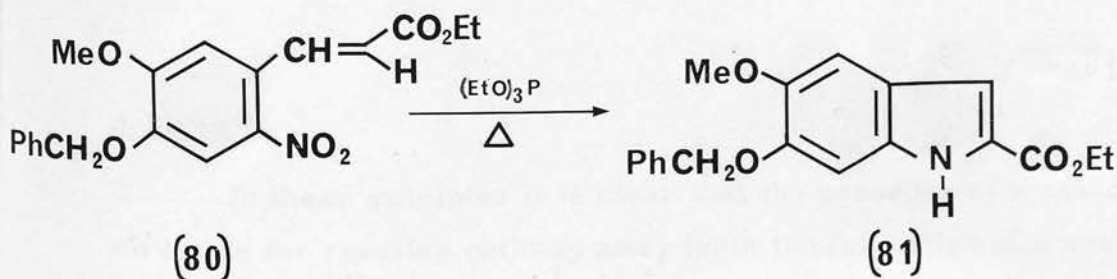
experiments, it is not clear if this was a genuine photochemically induced deoxygenation.

Kametani and his co-workers^{44d} cleverly employed the reaction in an attempted synthesis of rutaecarpine (77). This reaction would involve the formation of an indole nucleus with concomitant rearrangement, as observed by Sundberg³⁹ in his investigations of β, β -disubstituted-2-nitrostyrenes. Unfortunately in this case, the "wrong" substituent shifted giving an isomer which Kametani called pseudorutaecarpine (78) (Scheme 43). Also obtained was the aniline derivative (79), formed from the nitrene by hydrogen abstraction, followed by N-ethylation by triethyl phosphate.



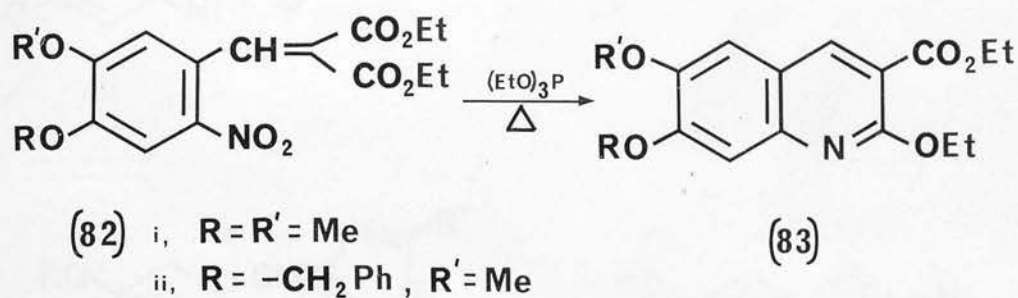
Scheme 43

Kametani and his co-workers^{44a} also extended Cadogan's synthesis³⁴ of ethyl indole-2-carboxylate, by deoxygenating the ethyl ester of 4,5-dialkoxy-2-nitrocinnamic acid (80), from which they obtained a 56% yield of the ethyl indole-2-carboxylate (81) (Scheme 44).



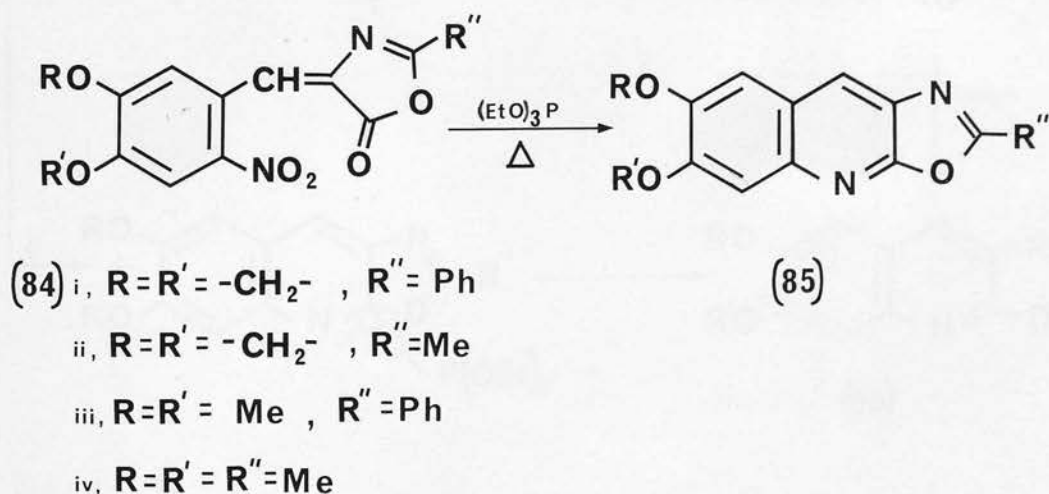
Scheme 44

However, when 4,5-dialkoxy-2-nitrobenzylidene malonate (82) was subjected to the same deoxygenation conditions,^{44a, c} a novel reaction occurred to give a quinoline derivative (83) in 53-68% yield (Scheme 45).



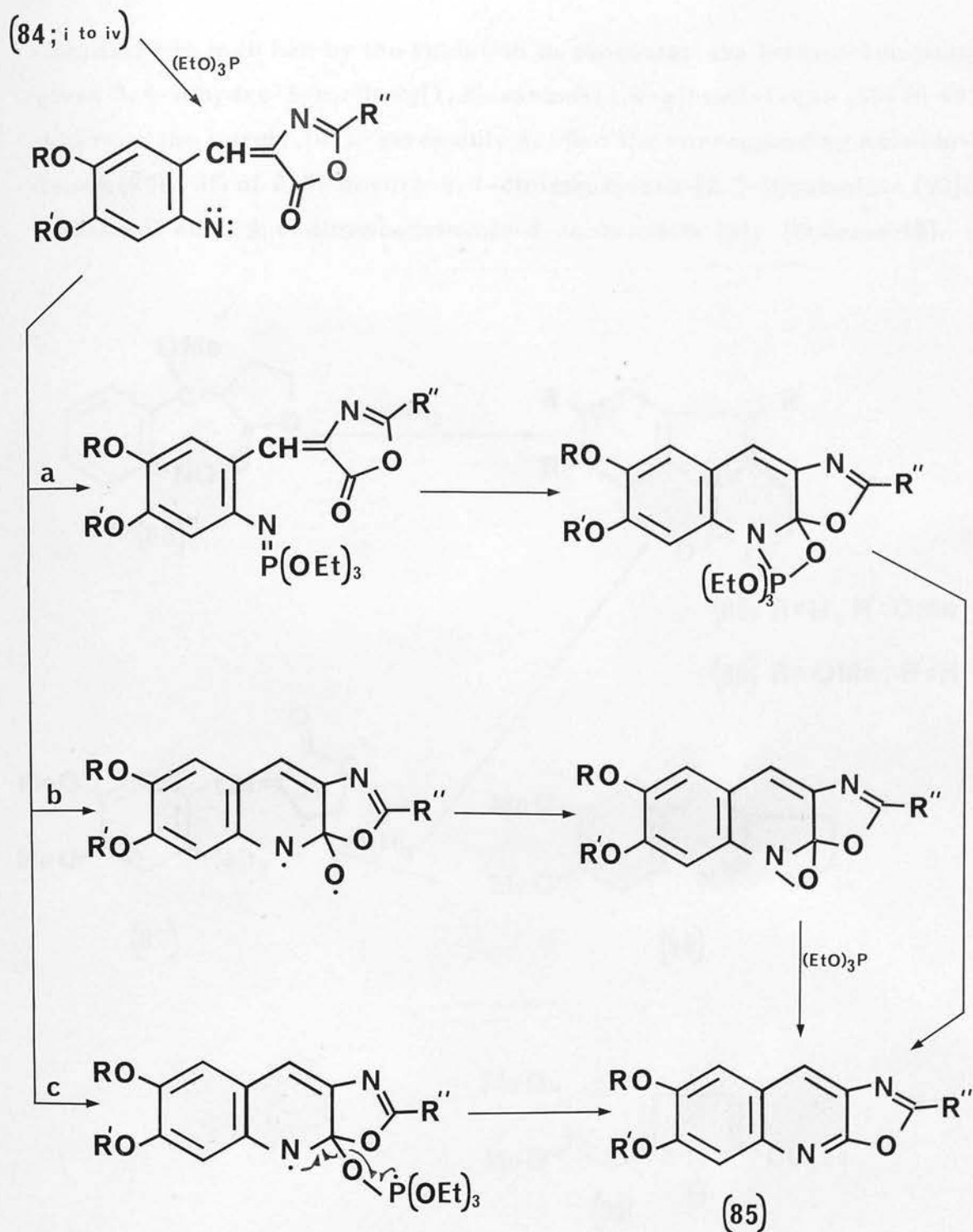
Scheme 45

Kametani and his co-workers^{44b} provided another example of this reaction when they reacted 2-substituted-4-(4,5-dialkoxy-2-nitrobenzylidene)oxazol-5-ones (84) with triethyl phosphite and obtained 2-substituted 6,7-dialkoxy-oxazolo-[5,4-b]quinolines (85) in yields of between 37.5 and 57% (Scheme 46).



Scheme 46

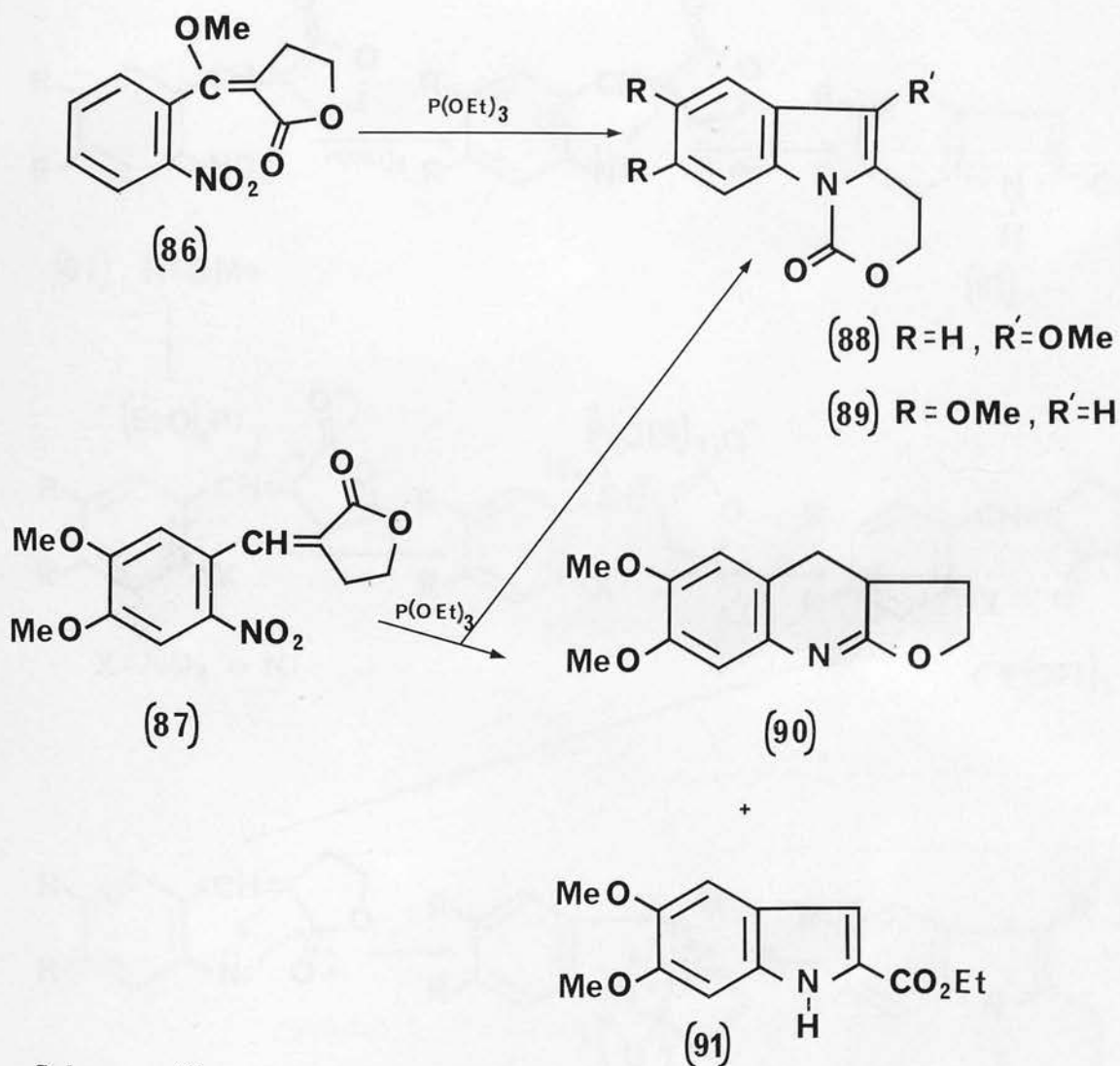
In these examples it is clear that the presence of a carbonyl group is diverting the reaction pathway away from the formation of a substituted indole, and Kametani^{44b} has suggested three possible routes to the oxazoloquinolines (Scheme 47), none of which involves the initial five-membered ring formation



Scheme 47

often favoured by nitrenes.^{6, 36} Kametani and his co-workers examined further related systems, including α -(2-hydroxyethyl)- β -methoxy-2-nitrocinnamic acid γ -lactone (86),^{44e} in which the carbonyl group and phenyl group are cis to each other, and 4,5-dimethoxy- α -(2-hydroxyethyl)-2-nitrocinnamic acid γ -lactone (87),^{44f} in which these groups are trans. The contrast in stereo-

chemistry is matched by the variation in products: the former compound (86), gives 3,4-dihydro-5-methoxy[1,3]oxazino-[3,4-a]indol-1-one (88) in 45% yield whereas the latter, (87), gives only 4.5% of the corresponding oxazino-indol-1-one (89), 3% of 2,3-dihydro-6,7-dimethoxyfuro-[2,3-b]quinoline (90), and a trace of ethyl 5,6-dimethoxyindole-2-carboxylate (91) (Scheme 48).

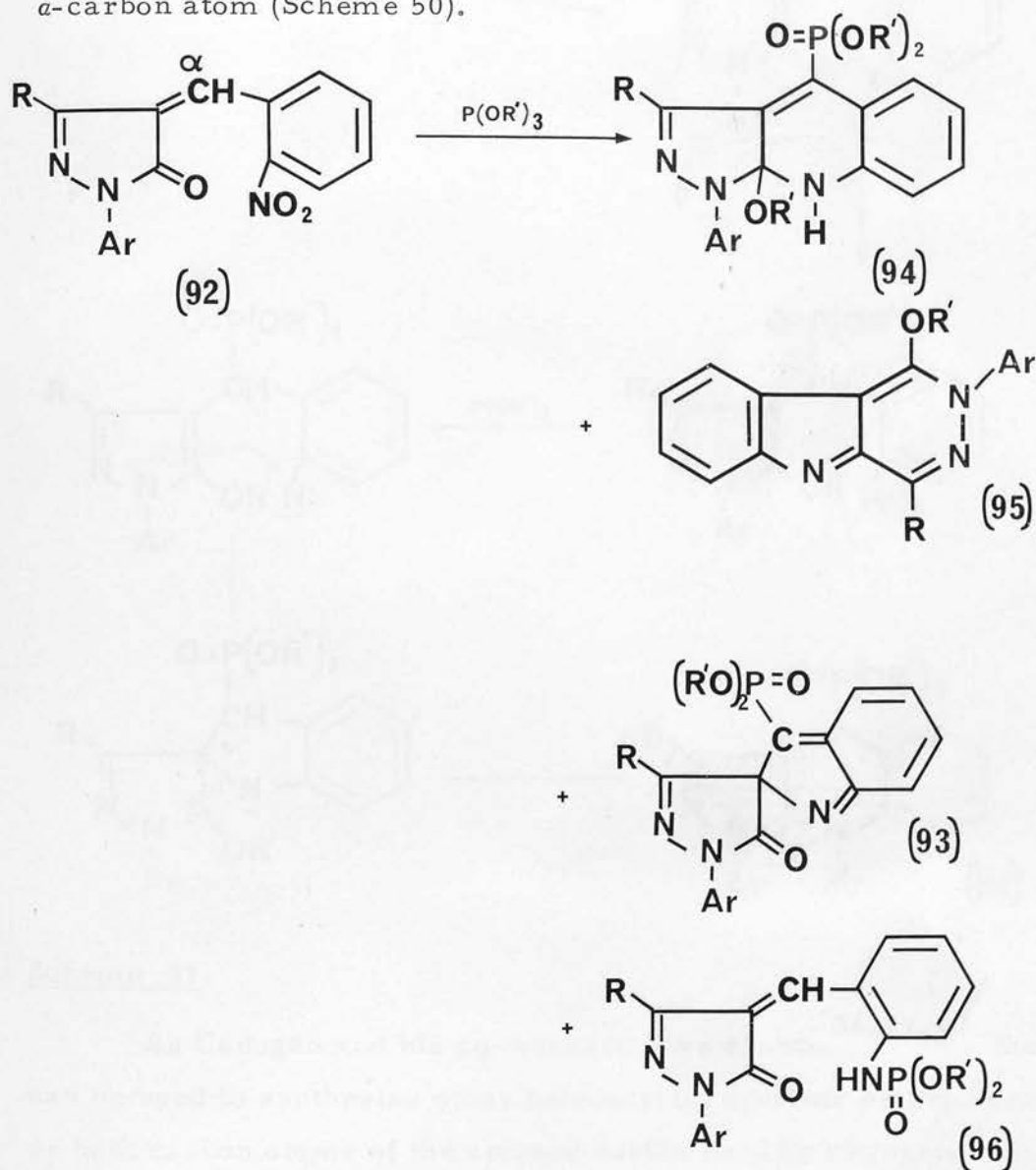


Scheme 48

To account for these products, Kametani has proposed a reaction scheme which, in the case of the latter compound (87), involves, effectively, the isomerisation of the double bond via reversible addition of a molecule of triethyl phosphite (Scheme 49). That this kind of nucleophilic attack on the double bond could occur is shown by the work of Nishiwaki and his co-workers,⁴ who investigated the deoxygenation of a related system, 3-alkyl-4-(2-nitro-

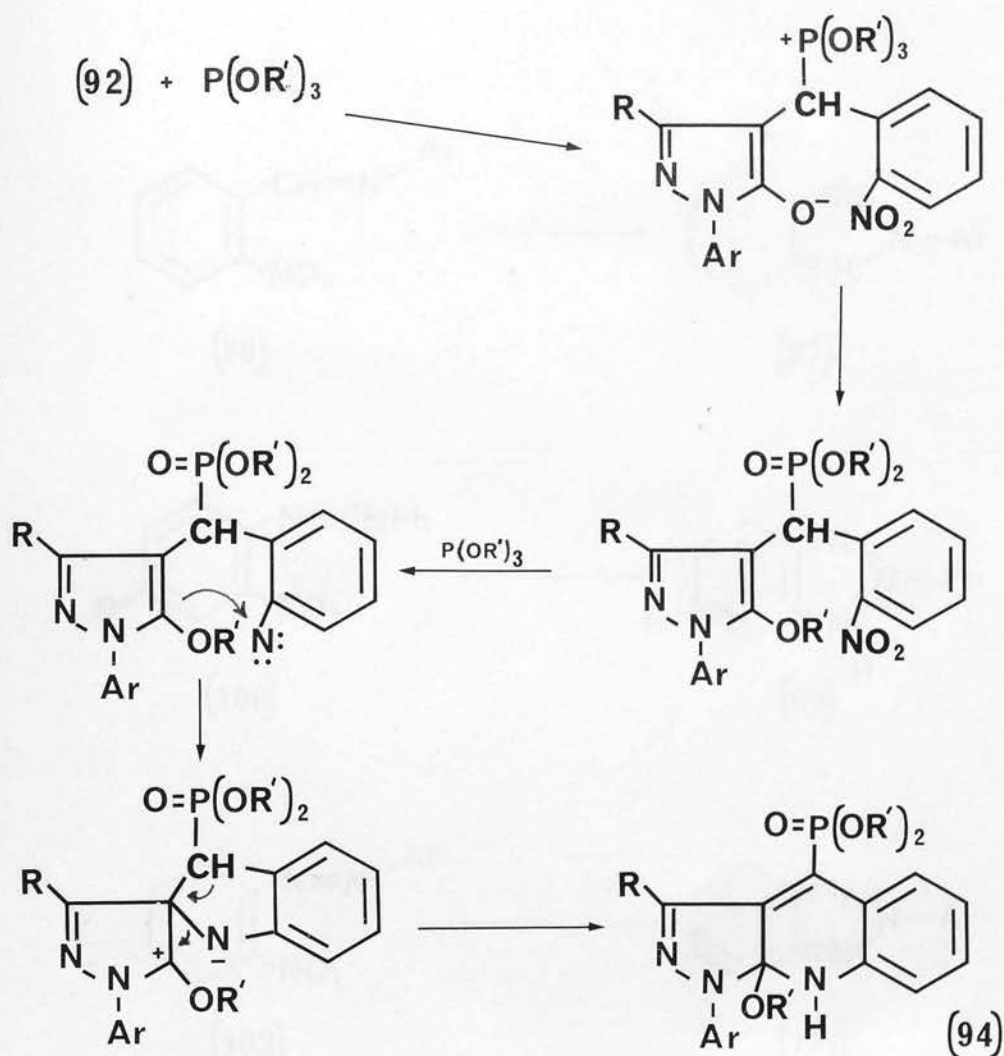
Scheme 49

benzylidene)-1-aryl- Δ^2 -pyrazolin-5-one (92), and isolated two products, among others, in which a phosphonate group was attached to the original α -carbon atom (Scheme 50).



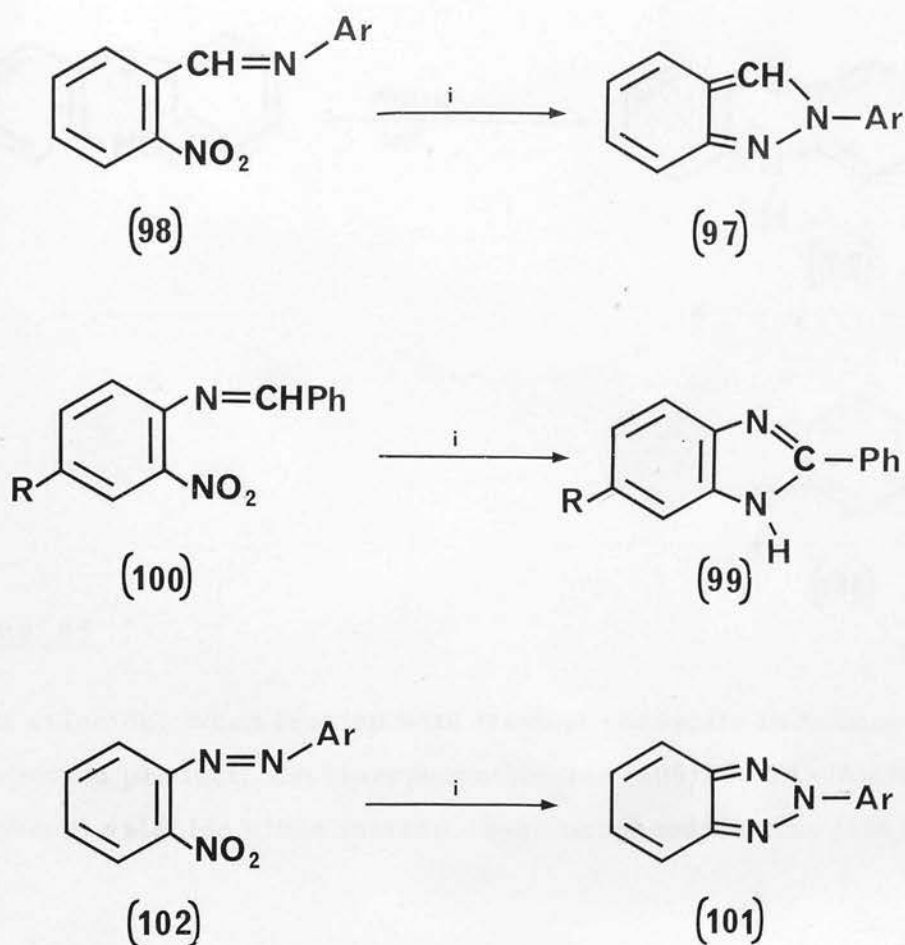
Scheme 50

The spiro-compound (93) was only obtained in trace amounts, but the dihydropyrazolo[3,4-*b*]quinolin-4-ylphosphonate derivative (94) was the major product, in 7 to 25% yield. Nishiwaki proposed the following mechanisms to account for its formation (Scheme 51). The 2H-pyridazino[4,5-*b*]indole (95) was obtained in 3 to 4% yield in only two cases, and, similarly, only traces of the phosphoramidate (96) were obtained, except when $R = Ar = \text{phenyl}$, in which case the yield was 48%.



Scheme 51

As Cadogan and his co-workers have shown,^{34, 47, 48} the reaction can be used to synthesize other heterocyclic systems by replacement of one or both carbon atoms of the styrene double bond by nitrogen. In this way 2H-indazoles (97; 34-83.5%) have been prepared from 2-nitroanils (98),³⁴ 2-phenylbenzimidazoles (99; 33-47%) have been prepared from N-benzylidene-2-nitroanilines (100),⁴⁸ and 2H-benzotriazoles (101; 31-72.5%) from 2-nitroazobenzenes (102),³⁴ (Scheme 52).



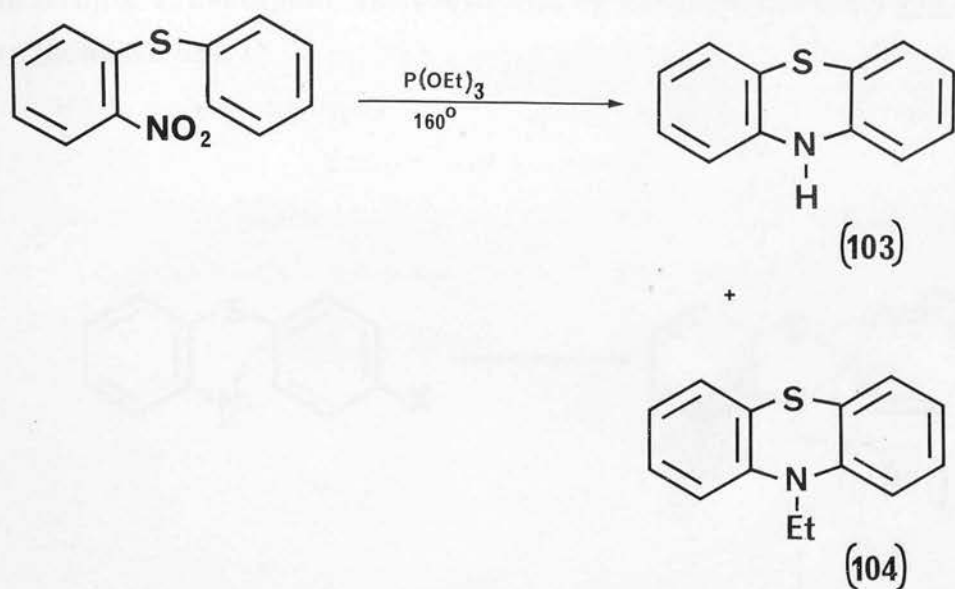
Scheme 52

i = $\text{P}(\text{OEt})_3$: 160°

A. 2. (d) Deoxygenation of Aryl 2-Nitrophenyl Sulphides and Related Compounds

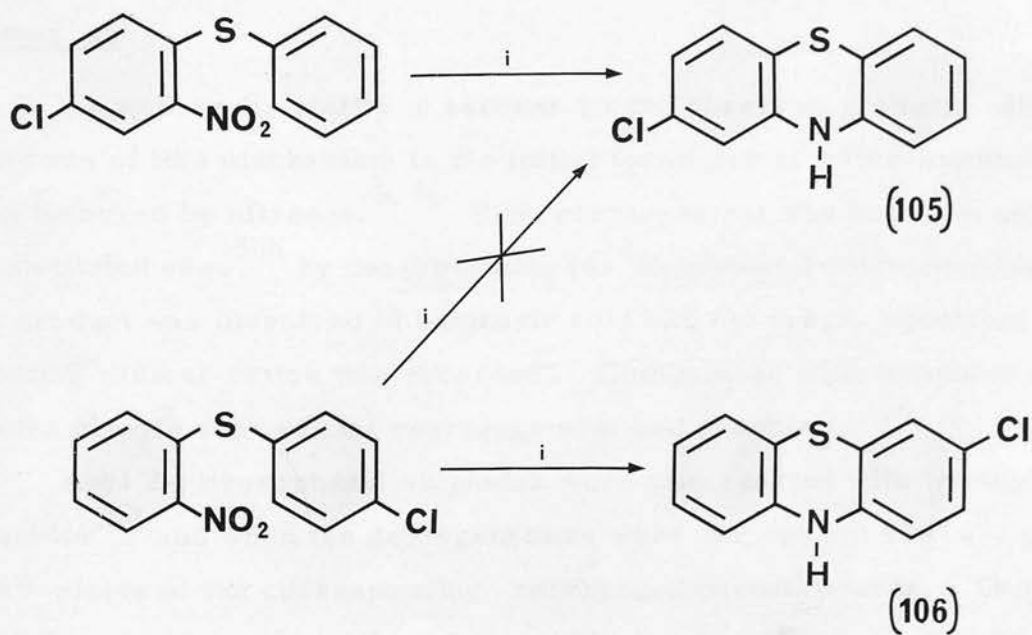
In 1966 Cadogan and his co-workers⁴⁹ reported that deoxygenation of 2-nitrophenyl phenyl sulphide by triethyl phosphite gave phenothiazine (103) in 54% yield, plus 2% of the *N*-ethyl derivative (104), (Scheme 53).

At first sight this appears to involve insertion of a nitrene into the β -C-H bond to form the six-membered ring directly, but later studies on substituted aryl 2-nitroaryl sulphides,⁵⁰ which gave substituted phenothiazines in 50-85% yields, disproved this theory. For example, 2-nitro-4-chlorophenyl



Scheme 53

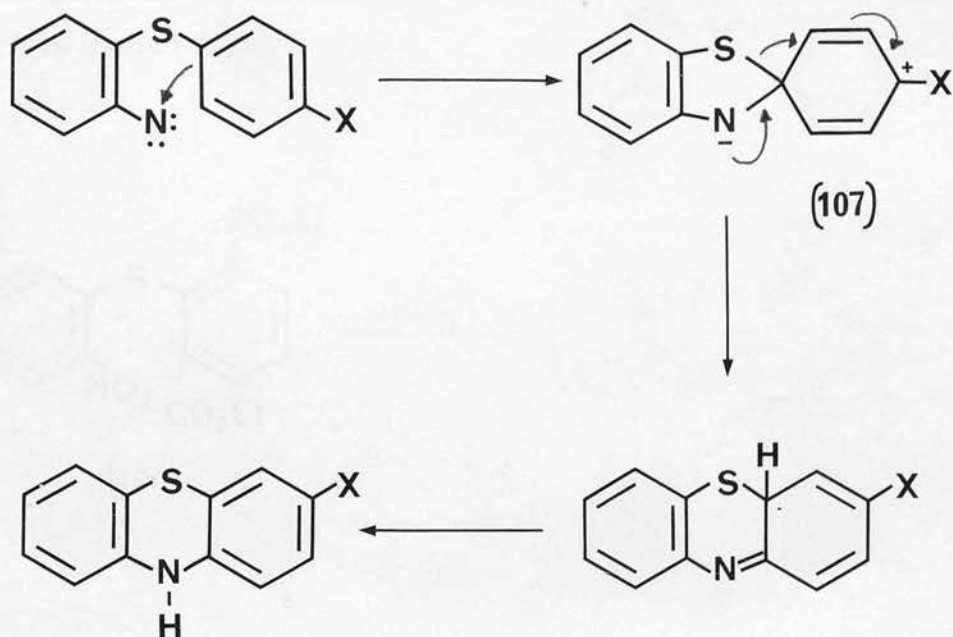
phenyl sulphide, when treated with triethyl phosphite in boiling cumene, gives the expected product, 2-chlorophenothiazine (105), but 4-chlorophenyl 2-nitrophenyl sulphide gives instead, 3-chlorophenothiazine (106), (Scheme 54).



i = P(OEt)_3 : 160°

Scheme 54

To account for the rearrangement in the latter case, Cadogan proposed a mechanism involving a spiro-dienyl intermediate (107), which undergoes a sigmatropic 1, 2-sulphur shift followed by re-aromatisation via a hydrogen shift (Scheme 55).



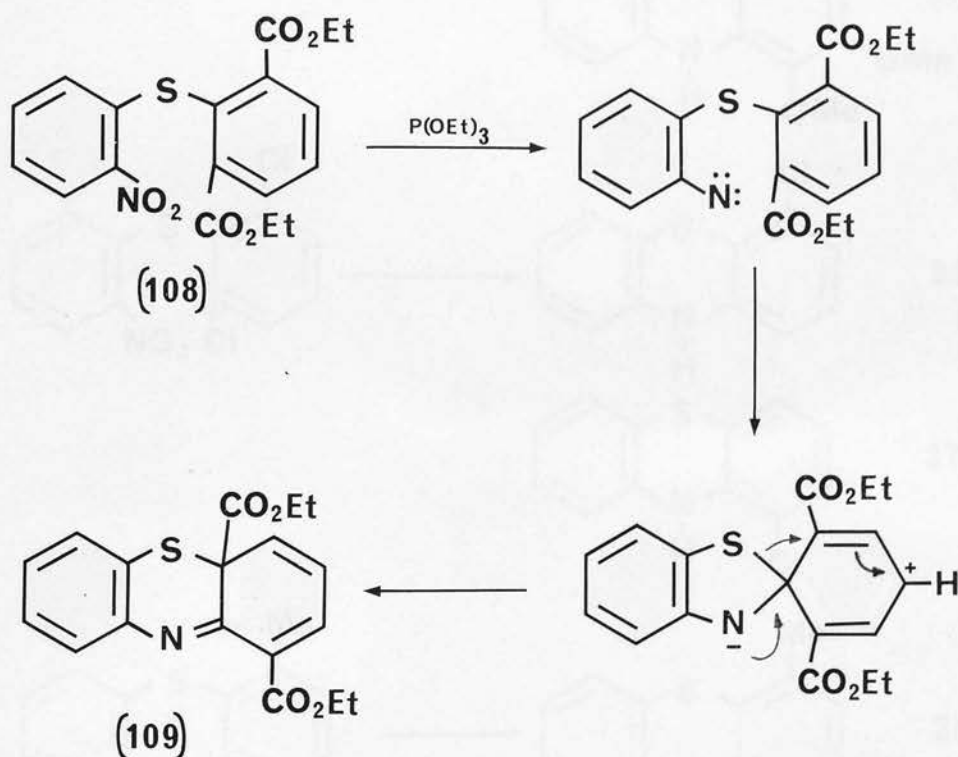
Scheme 55

As well as its ability to account for the observed products, an attraction of this mechanism is the initial formation of a five-membered ring, often favoured by nitrenes.^{6, 36} The rearrangement was shown to occur in the unsubstituted case^{50b} by deoxygenating [4-²H₁]phenyl 2-nitrophenylsulphide. The product was dissolved in sulphuric acid and the e. s. r. spectrum of the resulting radical-cation was recorded. Comparison with computer simulated spectra clearly showed that rearrangement had occurred.

Aryl 2-nitrosophenyl sulphides were also reacted with triethyl phosphite^{50d} and when the deoxygenations were carried out at 160°, gave 7-26% yields of the corresponding, rearranged phenothiazines. Occasionally a small yield of an unrearranged phenothiazine was observed, but this may have been a result of thermal cyclisation prior to deoxygenation. Deoxygenation of the nitroso-compounds at 0°C gave no phenothiazines, suggesting,

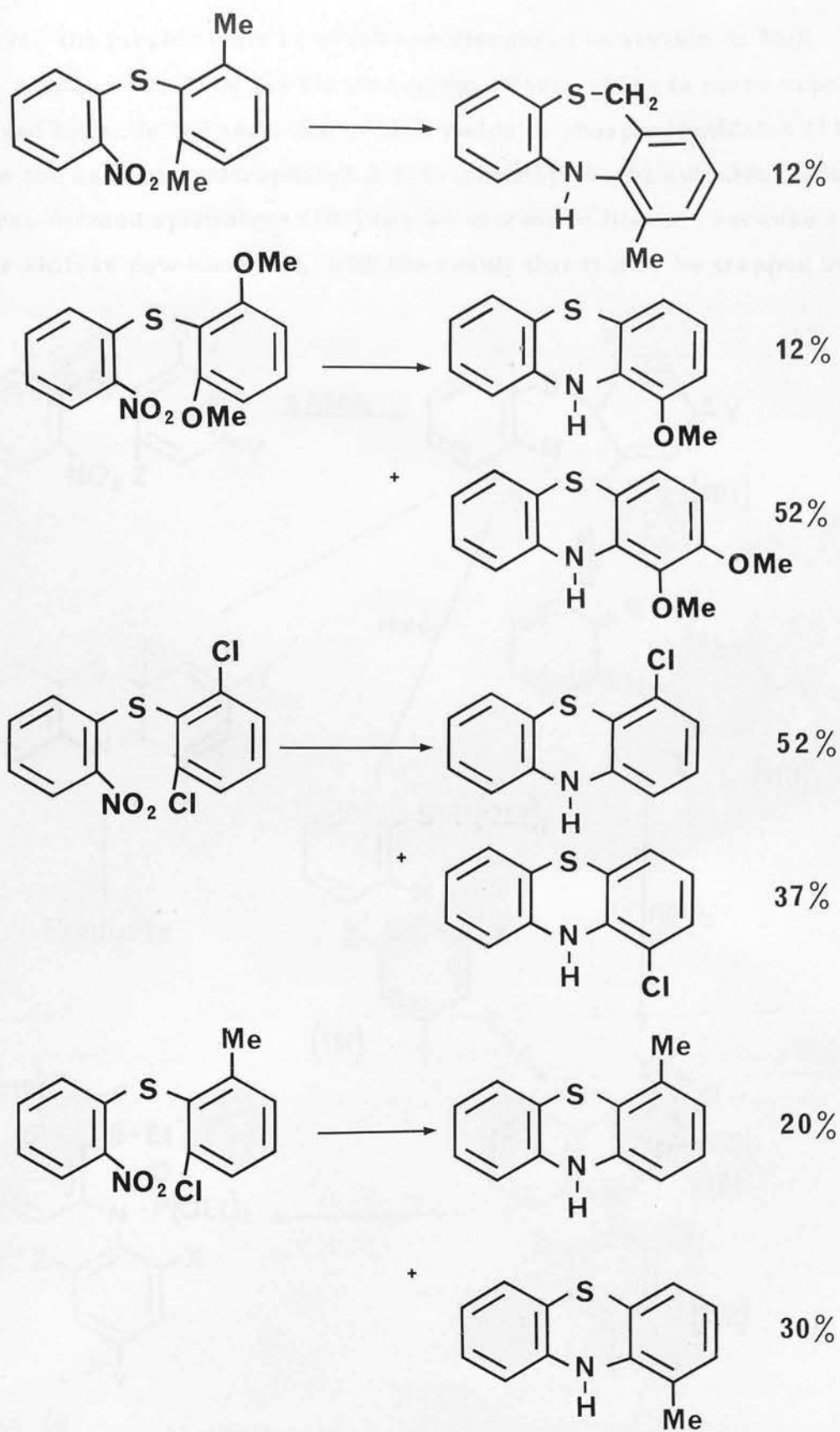
perhaps, that the shift of sulphur required an elevated temperature.

Cadogan's mechanism, (Scheme 55), involves as its final step, a 1,3-hydrogen shift. If both the ortho-positions of the appropriate benzene ring are substituted, it might be expected that rearomatisation is less likely to occur because of the decreased migratory aptitude of the substituent, relative to hydrogen. This indeed is observed⁵¹ in the case of 2,6-dicarboethoxyphenyl 2-nitrophenyl sulphide (108) which, on deoxygenation by triethyl phosphite, gives 4aH-phenothiazine-1,4a-dicarboxylate diethyl ester (109), in 50% yield (Scheme 56).



Scheme 56

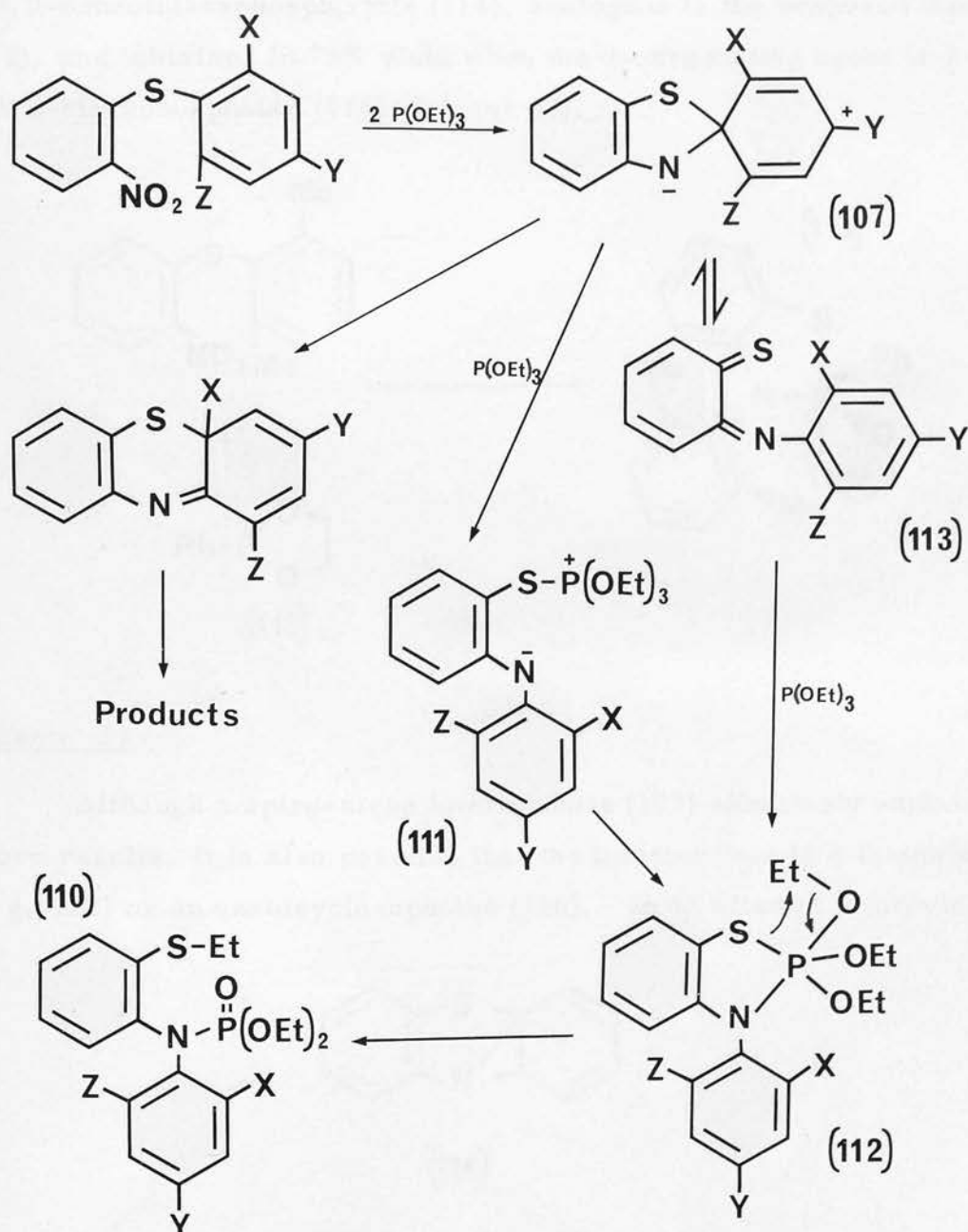
The isolation of this compound is further good evidence for the mechanism. The corresponding diaryl sulphides, 2,6-dimethyl, 2,6-dimethoxy, 2,6-dichloro, and 2-chloro-6-methyl, do not give compounds analogous to (109) however,⁵¹ but each reacts to give characteristic products (Scheme 57). A discussion of the "blocked-ortho" effect in section A.3(b) includes details of the mechanisms of the first two examples. The products in the second two examples may arise from competition between nitrene and "nitrenoid"



Scheme 57

pathways, the mechanisms of which are discussed in section A. 3(a).

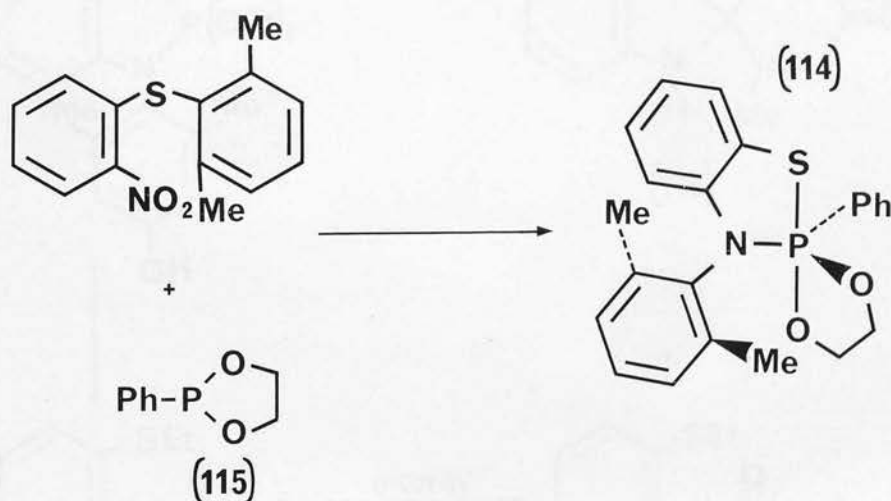
Another result of the blocked-ortho effect, which is more appropriately discussed here, is the isolation of high yields of phosphoramidates (110),^{51, 52} (77% in the case of 2-nitrophenyl 2,4,6-trimethylphenyl sulphide), (Scheme 58). The first-formed spirodiene (107) has an increased lifetime because a 1,2-sulphur shift is now hindered, with the result that it may be trapped by triethyl



Scheme 58

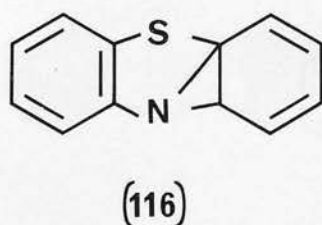
phosphite, rather than follow the previous route (Scheme 55) to a phenothiazine derivative. Trapping may occur by nucleophilic attack of phosphite

on sulphur to give a zwitterion (111) which ring-closes to give the 1, 3, 2-benzothiazaphosph(v)ole (112), which, alternatively, may be formed by concerted addition of phosphite to the thioquinone imine isomer (113) of the spiro-diene. The isolated phosphoramidates (110) are then formed by simple intramolecular rearrangement of the 1, 3, 2-thiazaphosph(v)ole (112), as shown in Scheme 58. In support⁵³ of this mechanism is the isolation of a stable 1, 3, 2-benzothiazaphosph(v)ole (114), analogous to the proposed intermediate (112), and obtained in 73% yield when the deoxygenating agent is 2-phenyl-1, 3, 2-dioxaphospholan (115) (Scheme 59).

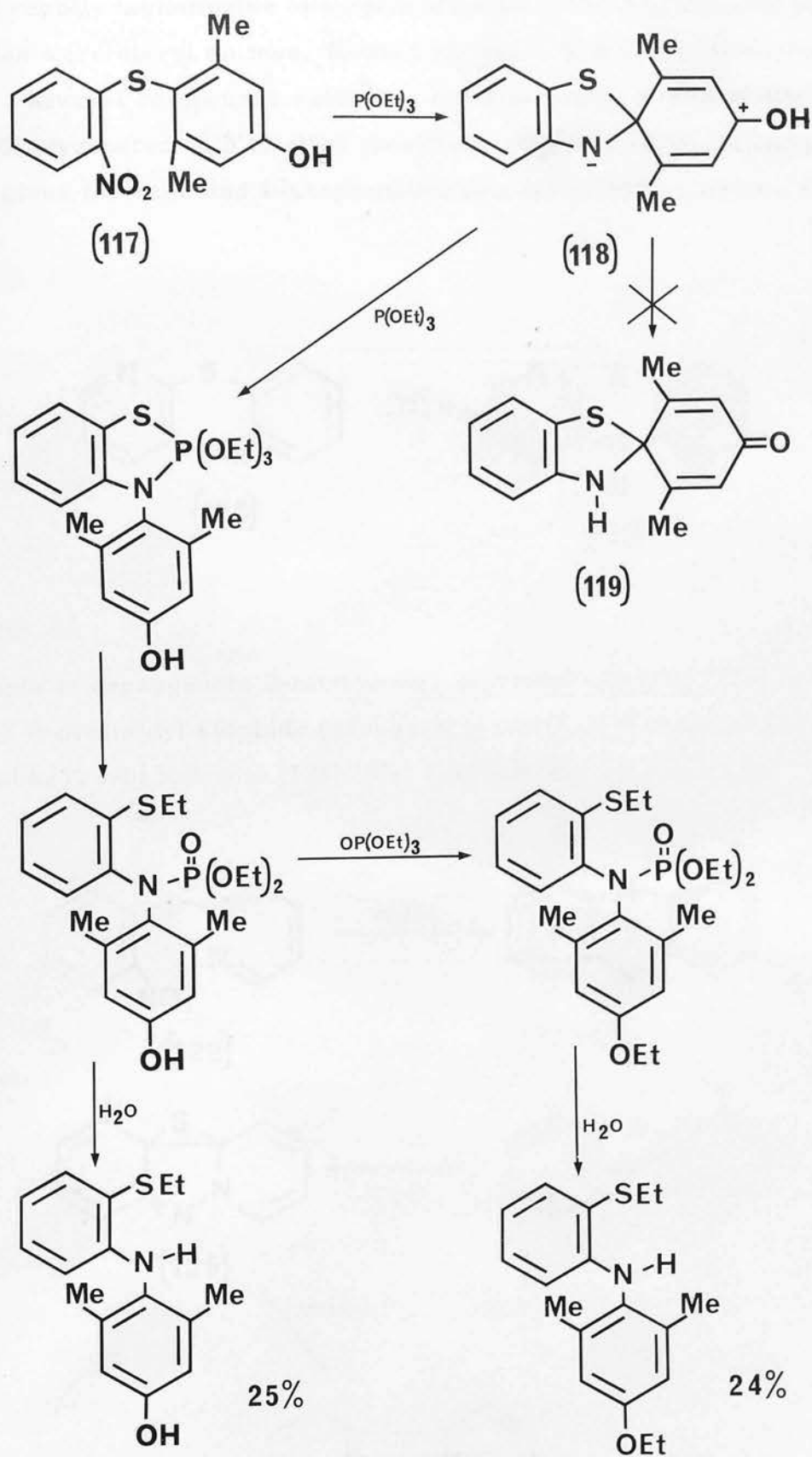


Scheme 59

Although a spiro-diene intermediate (107) effectively explains the above results, it is also possible that the intermediate is a thioquinone imine (e. g. 113) or an azabicyclo-species (116). In an attempt to provide evidence



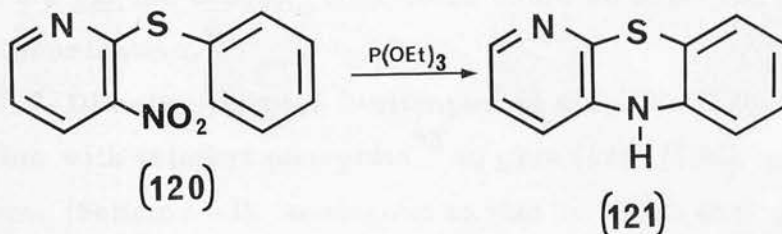
in favour of the spirodiene species, Cadogan and Tait⁵² deoxygenated 2, 6-dimethyl-4-hydroxyphenyl 2-nitrophenyl sulphide (117) with triethyl phosphite. It might be expected that a spiro-diene system such as (118; Scheme 60)



Scheme 60

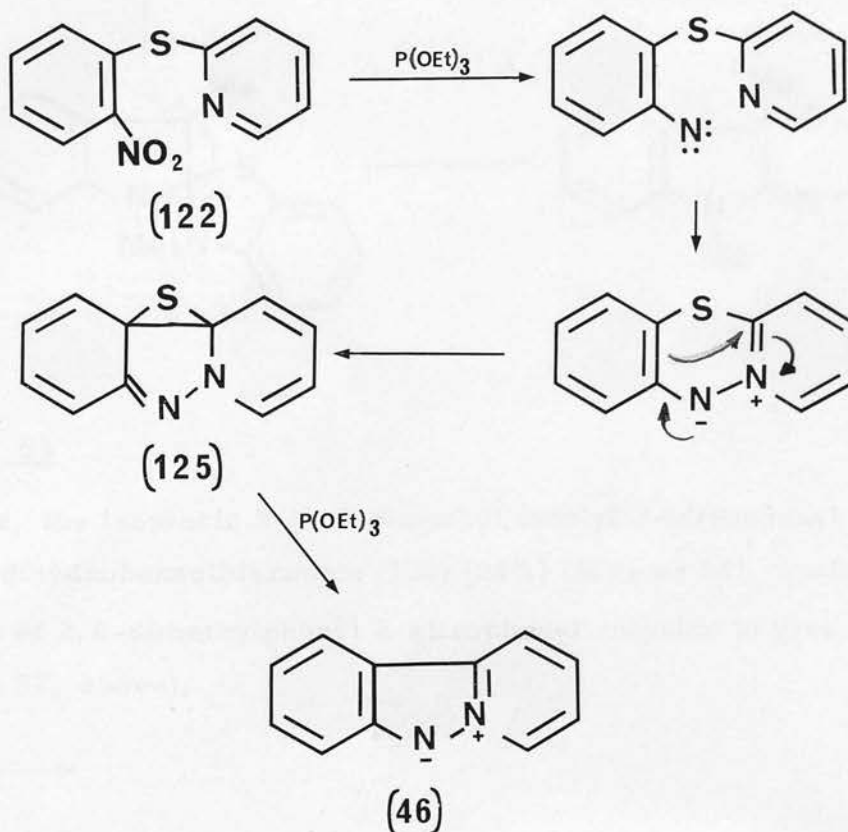
would readily tautomerise to a spiro-dienone (119), but the only products isolated were diaryl amines, formed via the 1, 3, 2-benzothiazaphosph(v)ole.

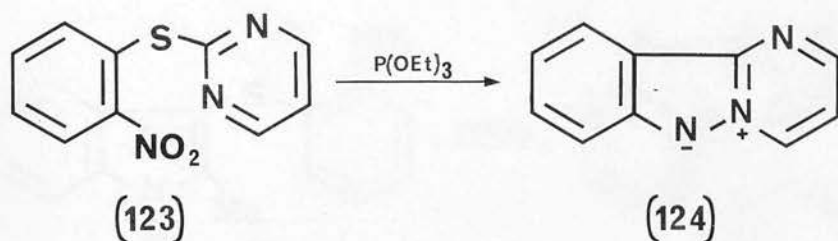
Several compounds related to the 2-nitroaryl aryl sulphides have been deoxygenated with triethyl phosphite. 3-Nitro-2-thiophenylpyridine (120) gives the expected 4-azaphenothiazine (121) (30%) (Scheme 61),⁵⁴ but



Scheme 61

attempts to deoxygenate 2-nitrophenyl 2-pyridyl sulphide (122) and 2-nitrophenyl 2-pyrimidyl sulphide (123) gave pyrido[1, 2-b] indazole (46) (2%) and pyrimido[1, 2-b] indazole (124) (5%) respectively (Scheme 62). The products

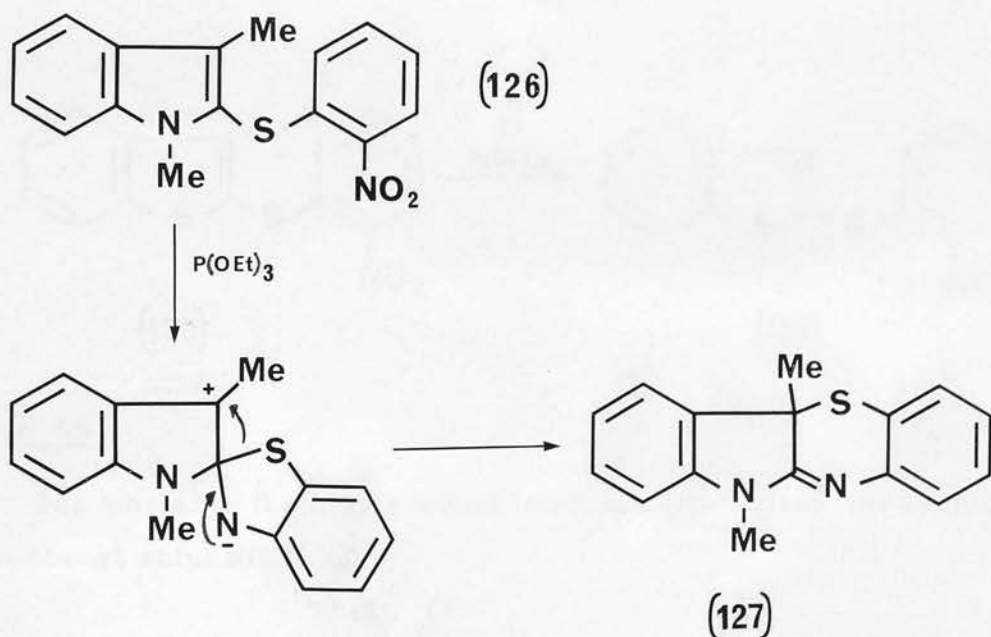




Scheme 62

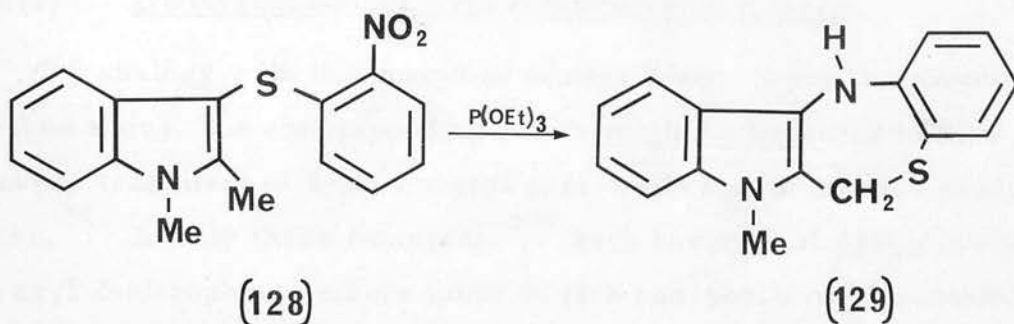
probably arise via the thiiran (125) which could be expected to undergo ready desulphurisation.⁶

2-(1,3-Dimethyl)indolyl 2-nitrophenyl sulphide (126) undergoes deoxygenation with triethyl phosphite⁵⁵ to give (127), (70%), presumably via a mechanism, (Scheme 63), analogous to that in which 4aH-phenothiazine-1,4a-dicarboxylate diethyl ester (109), is formed (Scheme 56, above).



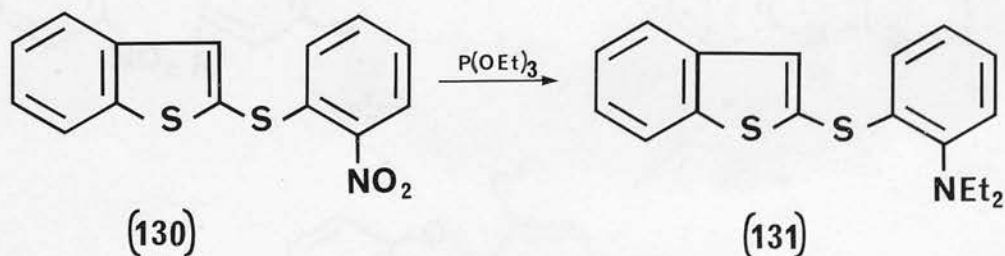
Scheme 63

However, the isomeric 3-(1,2-dimethyl)indolyl 2-nitrophenyl sulphide (128) gives a dihydrobenzothiazepine (129) (34%) (Scheme 64), analogous to the reaction of 2,6-dimethylphenyl 2-nitrophenyl sulphide to give a thiazepine (Scheme 57, above).



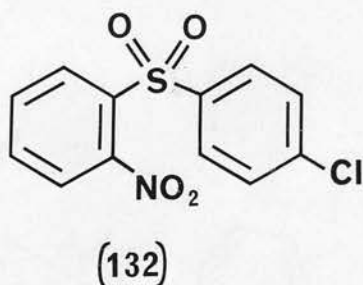
Scheme 64

Despite the differences in the final products, both of the above reactions appear to follow the general trend of initial formation of a spiro-dienyl intermediate. Deoxygenation⁵⁶ of the closely related 2-(2-benzo[b]thienylthio)nitrobenzene (130) gave no new heterocycle, but only 7% of the *N,N*-diethylaniline (131) and intractable tar (Scheme 65).



Scheme 65

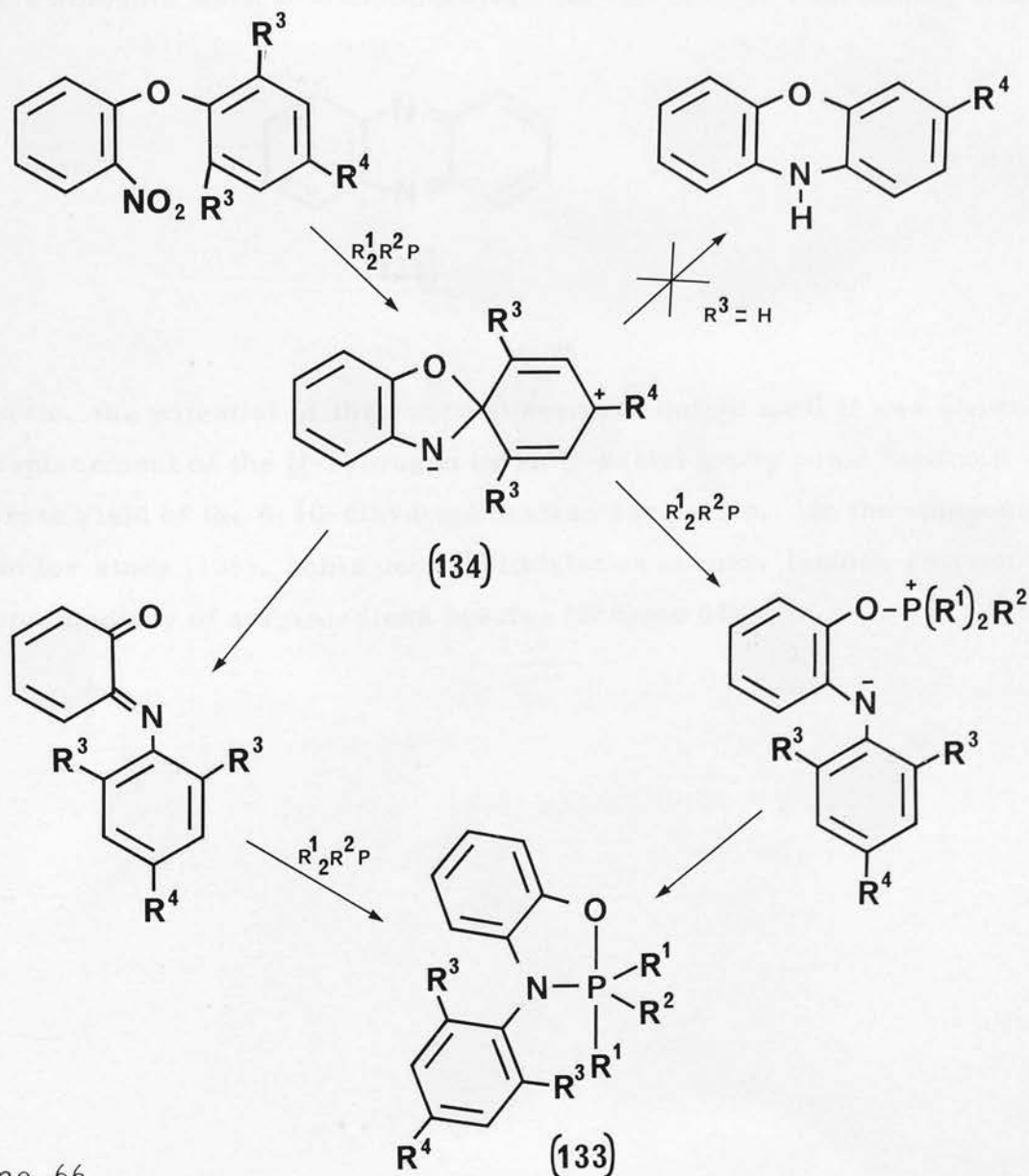
Tar was also the only product from deoxygenation⁵⁷ of 4-chlorophenyl 2-nitrophenyl sulphone (132).



A. 2. (e) Deoxygenation of Aryl 2-Nitrophenyl Ethers

By analogy with the reactions of aryl 2-nitrophenyl sulphides, described above, the corresponding ethers might be expected to give phenoxazines. However, treatment of 2-nitrophenyl phenyl ether with triethyl phosphite yields only tar.³⁴ In only three examples,^{58a} each having both ortho-positions blocked, were aryl 2-nitrophenyl ethers found to give non-phosphorus-containing heterocycles, and then only in 1-5% yields. These reactions are described, together with those of the corresponding sulphides in section A. 3(b).

Nevertheless, the isolation⁵⁸ of 3-aryl-2, 3-dihydro-1, 3, 2-benzoxazaphosph(v)oles (133), in yields of between 12 and 95% from the reaction of a range of ethers and tervalent phosphorus reagents, is of great interest, and shows that there is a close analogy with the sulphide deoxygenations (Scheme 66). The

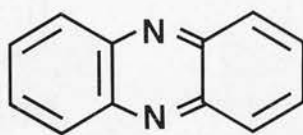


Scheme 66

mechanism of formation of the benzoxazaphosph(v)oles (133) proposed by Cadogan and his co-workers,⁵⁸ involves the spiro-diene (134) which, because of the lower migratory aptitude of oxygen as compared to sulphur, is trapped by phosphite before it can rearrange to a phenoxazine derivative. The benzoxazaphosph(v)oles are thermally stable, unlike the corresponding benzothiazaphosph(v)oles in which the nucleophilic sulphur is readily ethylated by an intramolecular mechanism (Scheme 58). The chemistry of the oxazaphosph(v)oles has now come under study, and is described in section B. 2.

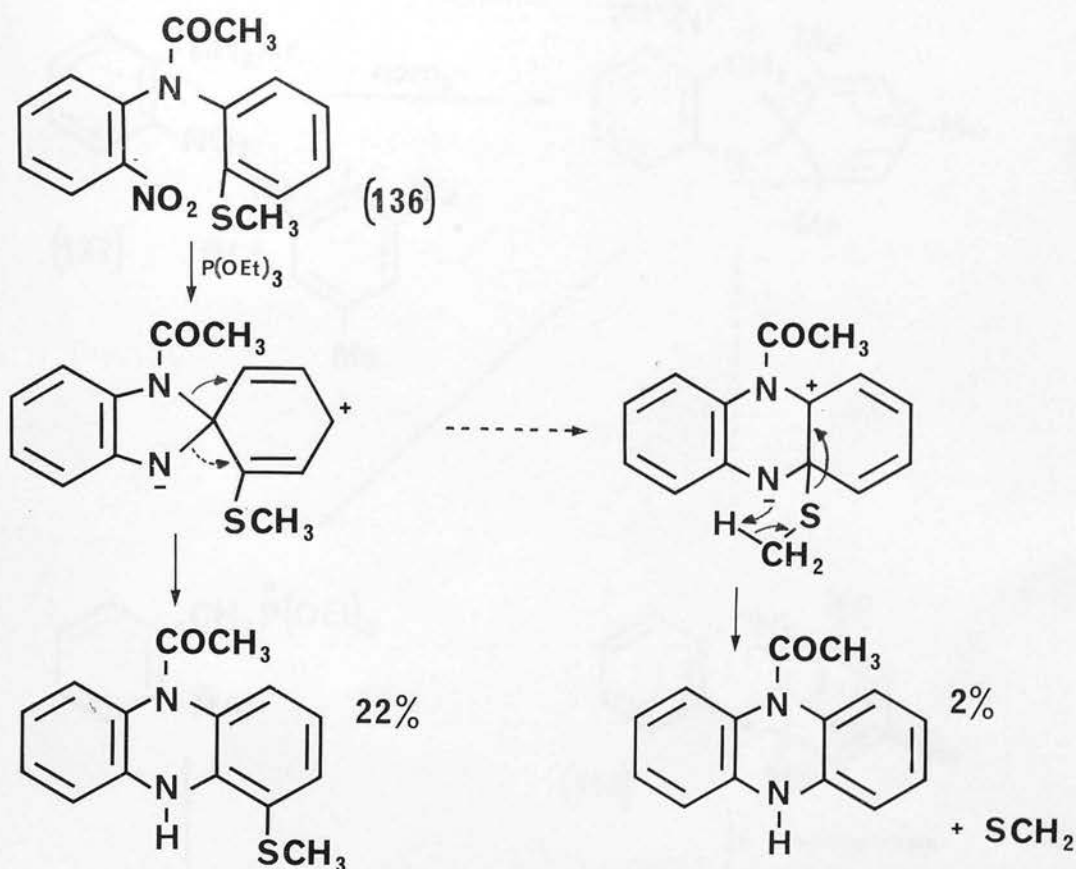
A. 2. (f) Deoxygenation of Miscellaneous Nitro-compounds

Although an early report³⁴ stated that phenazine (135) was obtained in trace amounts when 2-nitrodiphenylamine was treated with boiling triethyl



(135)

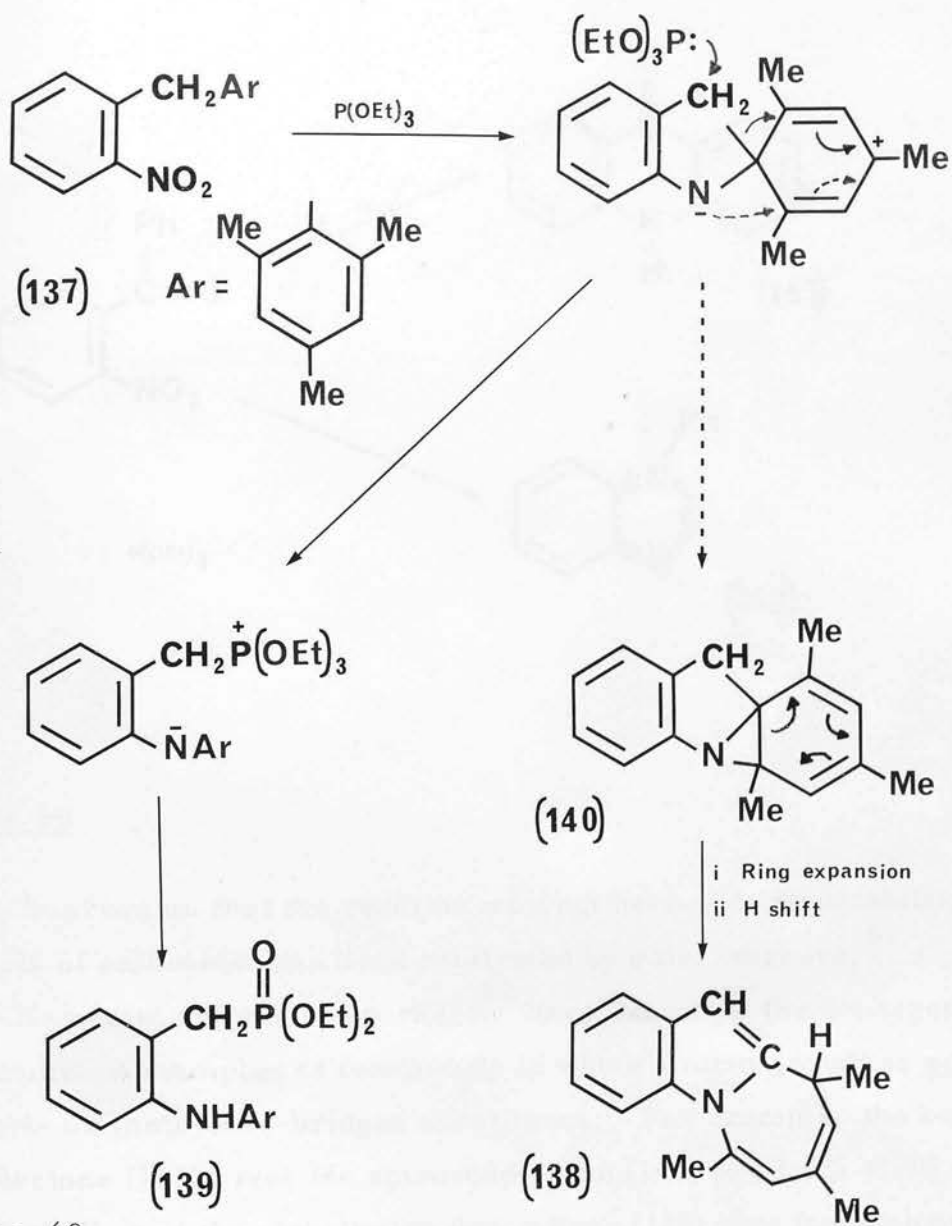
phosphite, the potential of the reaction seemed limited until it was shown⁵⁹ that replacement of the N-hydrogen by an N-acetyl group could lead to a moderate yield of the 5, 10-dihydrophenazine derivative. In the compound chosen for study (136), some demethylthiylation occurs, lending support to the intermediacy of a spiro-diene species (Scheme 67).



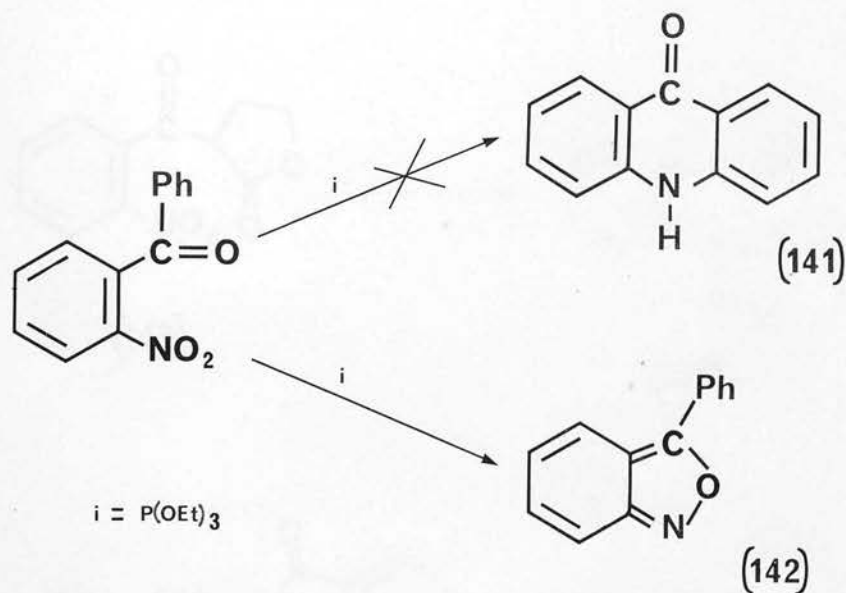
Scheme 67

1-(2-Nitrobenzyl)-2,4,6-trimethylbenzene (137), when deoxygenated with triethyl phosphite,^{58b} gives a mixture of azepinoindoles (e.g. 138), plus 7% of the substituted diethylbenzylphosphonate (139). The formation of the latter compound provides circumstantial evidence for a spiro-diene intermediate, and the formation of azepinoindoles, by thermolysis of 1-(2-azido-benzyl)-2,4,6-trimethylbenzene,⁶⁰ can be explained by the postulation of an azanorcaradiene intermediate (140), (Scheme 68).

The deoxygenation of 2-nitrobenzophenone⁴⁸ does not give acridone (141), but 3-phenyl-anthranil (142) in 56% yield, in addition to 19% of 2-aminobenzophenone (Scheme 69). However 2-nitroacetophenone gives only 19% of $\underline{\text{N}}$ -(2-acetylphenyl) phosphoramidate, $\underline{\text{o}}\text{-CH}_3\text{CO.C}_6\text{H}_4\text{.NH.P(O)(OEt)}_2$,



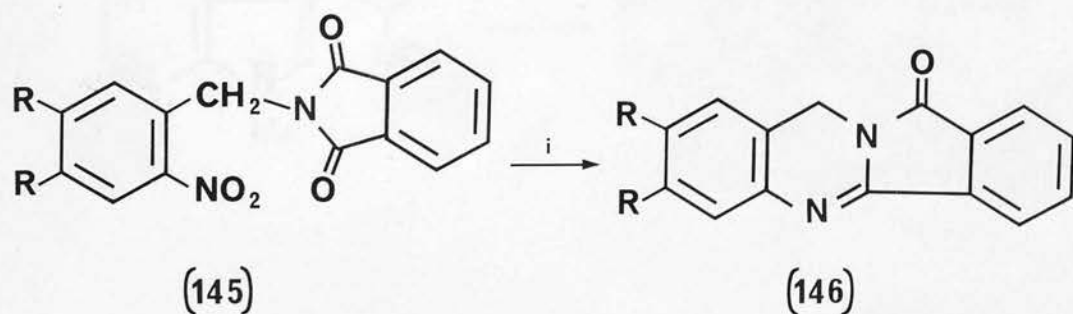
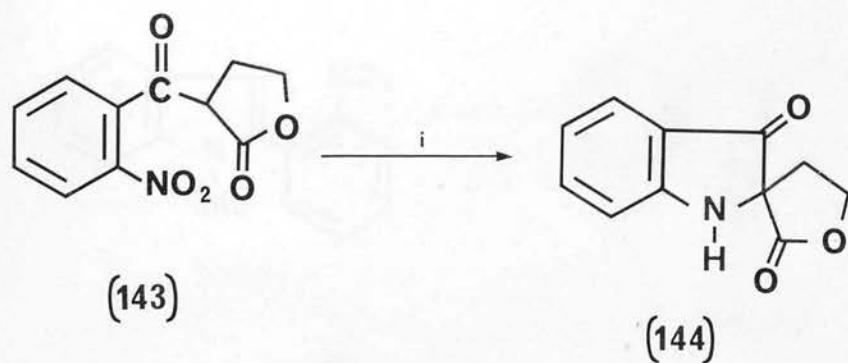
Scheme 68



Scheme 69

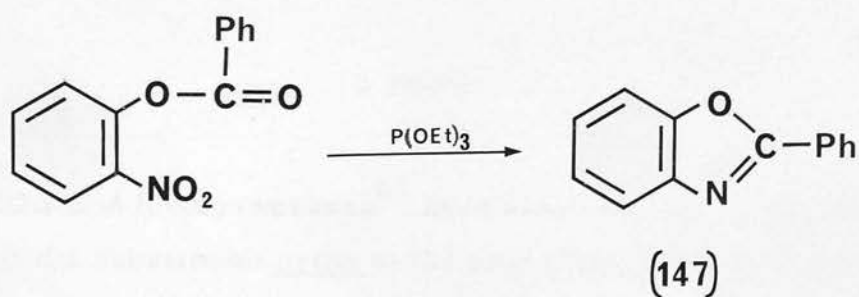
and the impression that the reaction may not have wide applicability as a synthesis of anthranils has been confirmed by other workers.⁶¹

Kametani and his co-workers⁶² have examined the deoxygenation of more complex examples of compounds in which a nitro-group is ortho to a carbonyl- or methylene-bridged substituent. For example, the benzoyl-butyrolactone (143) gives the spiro-compound (144) in 12.5% yield rather than the anthranil, and the phthalimide derivatives (145) give isoindoloquinazolines (146) in 17% (R≠OMe) or 21% (R=H) yield (Scheme 70). In the latter case, the concomitant deoxygenation of both the carbonyl and nitro-group is probably achieved by a mechanism analogous to that described in Scheme 47, for the formation of oxazolo-[5,4-b]quinolines. Another example of the concomitant deoxygenation of a carbonyl and a nitro-group was reported by Saunders,^{63a} who found that 2-phenylbenzoxazole (147) was formed in 68% yield by treating 2-nitrophenylbenzoate with boiling triethyl phosphite, (Scheme 71). 2-Nitrophenylacetate reacts similarly to give 2-methylbenzoxazole^{63b} (6.5%).



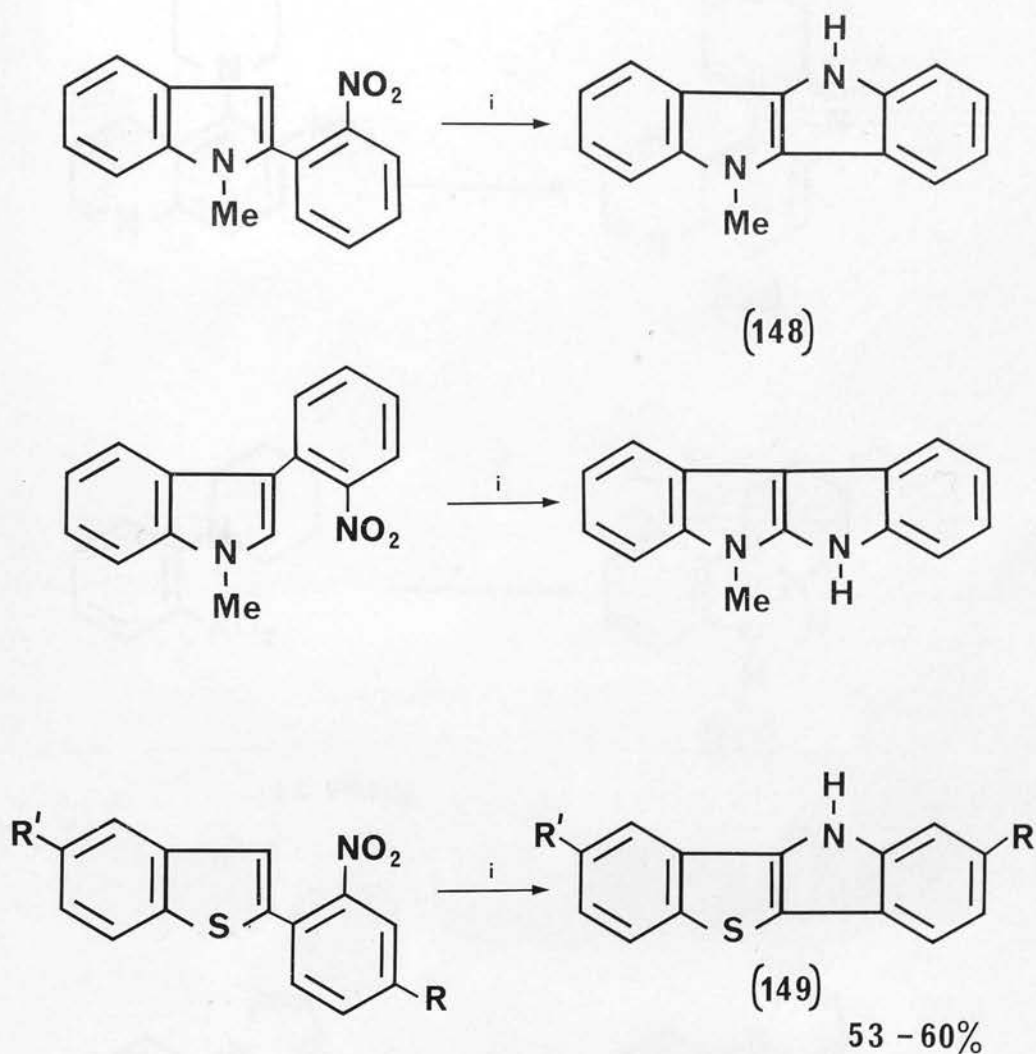
i = P(OEt)₃

Scheme 70



Scheme 71

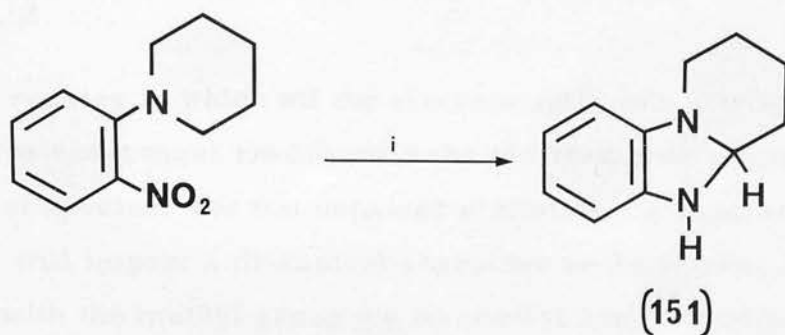
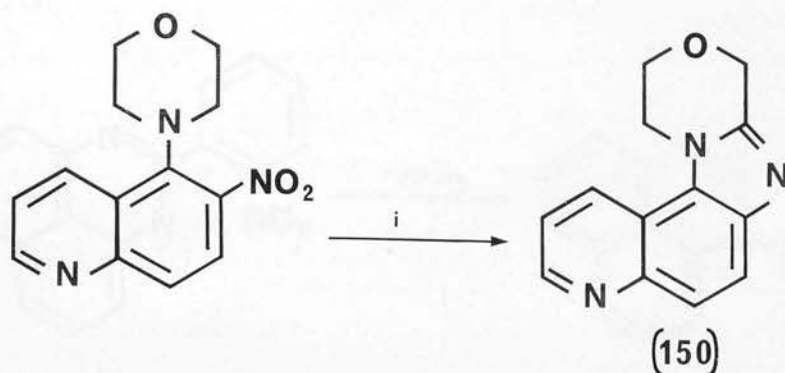
Deoxygenation reactions of 2- and 3-(2'-nitroaryl)indoles, which give indoloindoles (148),⁵⁵ and of 2-(2'-nitroaryl)benzothiophens, which give indolo-benzothiophens (149),⁶⁴ have been reported, and show no unusual mechanistic features (Scheme 72).



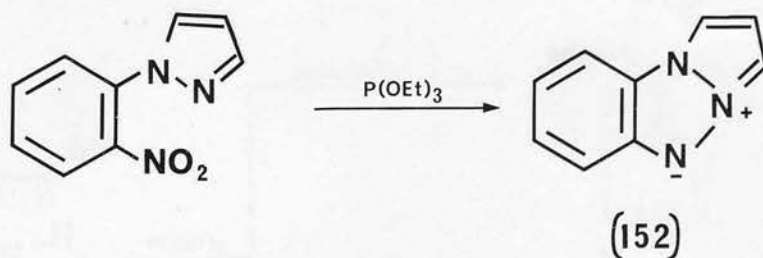
Scheme 72

Suschitzky and his co-workers⁶⁵ have also reported deoxygenation reactions in which the substituent ortho to the aryl nitro-group is a saturated heterocyclic system, and which lead, for example, to the formation of imidazoquinolines (e.g. 150) and dihydrobenzimidazoles: (e.g. 151), (Scheme 73).

A reaction analogous to the formation of pyrido[1,2-*b*]indazole (46) from 2-(2-nitrophenyl)pyridine, is the formation of pyrazolo[1,2-*a*]benzotriazole (152)⁶⁶ in 18% yield from 2-nitrophenylpyrazole (Scheme 74). Extensions⁶⁷ of this reaction, involving a cyclisation onto nitrogen, have led to the synthesis

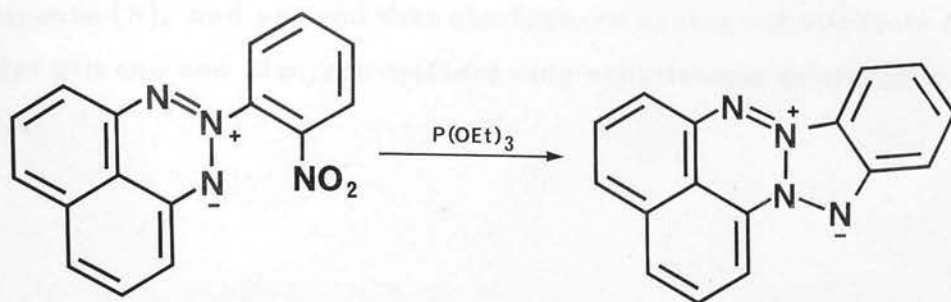


Scheme 73



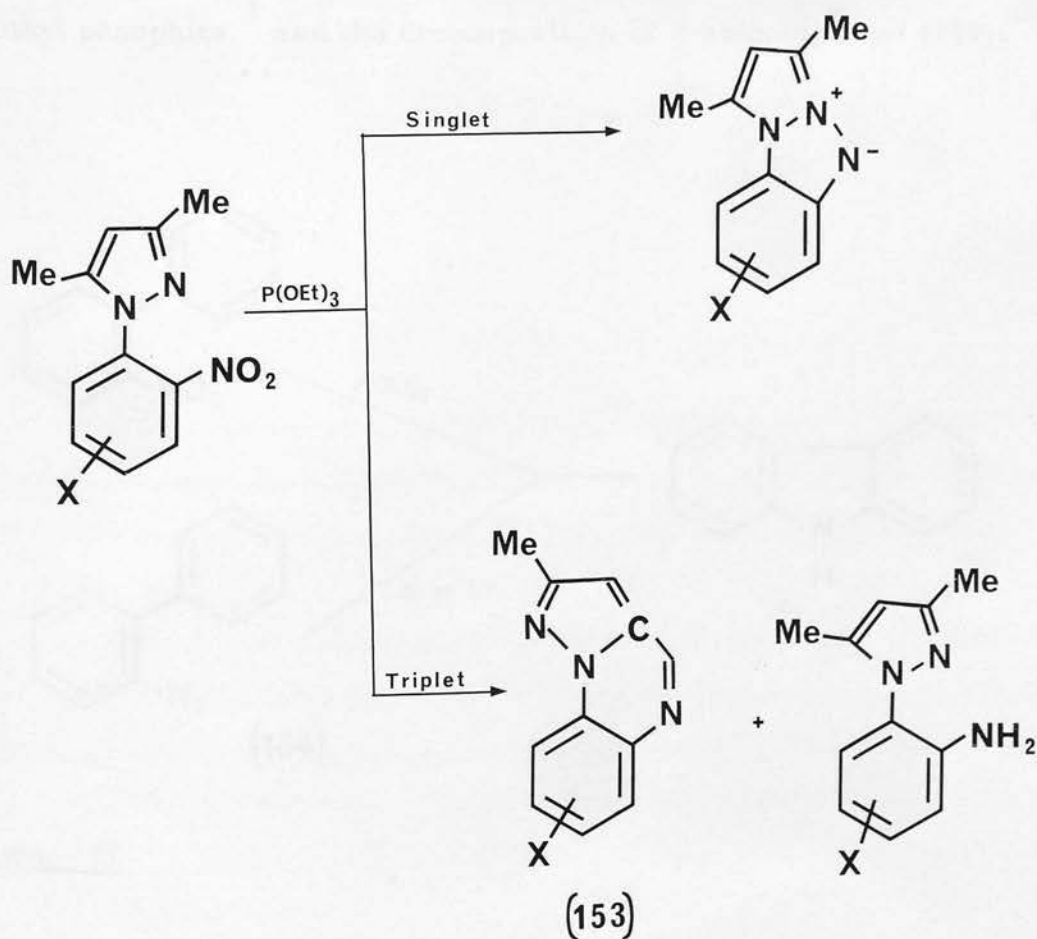
Scheme 74

of several tetra-aza polycyclic compounds (e.g. Scheme 75). Meth-Cohn and his co-workers⁶⁸ have employed this reaction to test for the intermediacy of singlet or triplet nitrenes during the deoxygenation of nitro-compounds. They have deoxygenated compounds related to 2-nitrophenylpyrazole in which the intermediate nitrene has the choice of cyclising to two quite different groups, a basic ring nitrogen or a saturated methyl group. If the nitrene is



Scheme 75

a singlet species in which all the electron spins are paired, it might be expected to react most readily with the electron-rich nitrogen, whereas if it is a triplet species, the two unpaired electrons, in separate molecular orbitals, will impart a di-radical character to the nitrene, permitting reaction with the methyl group via an abstraction/recombination mechanism. This is shown in Scheme 76, in which the isolated compound (153) has arisen by abstraction/recombination followed by oxidation.



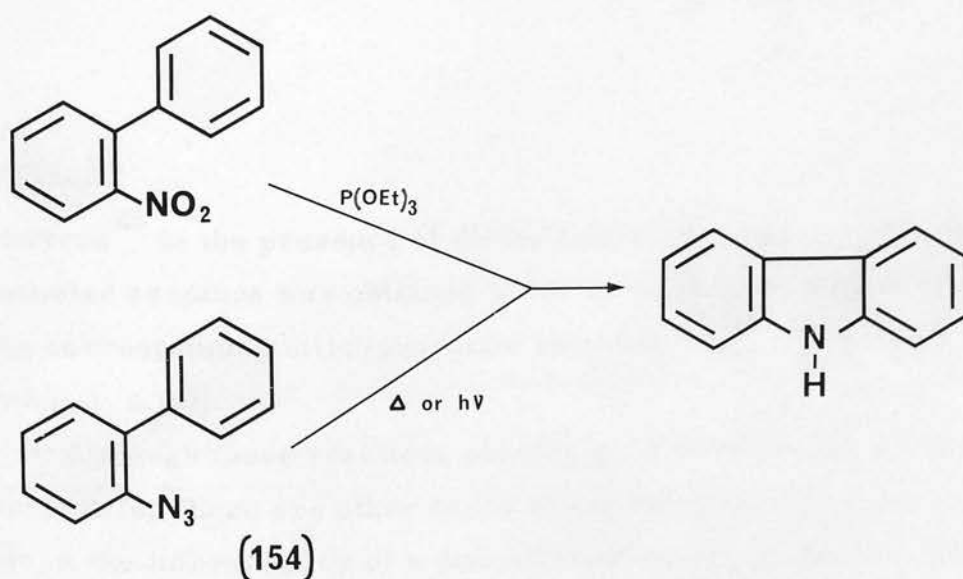
Scheme 76

The ratio of singlet to triplet products was measured for a range of substituents (X), and showed that electron-releasing substituents favoured a triplet nitrene and electron-withdrawing substituents favoured a singlet nitrene.

A. 3. (a) The Question of Nitrene Intermediacy

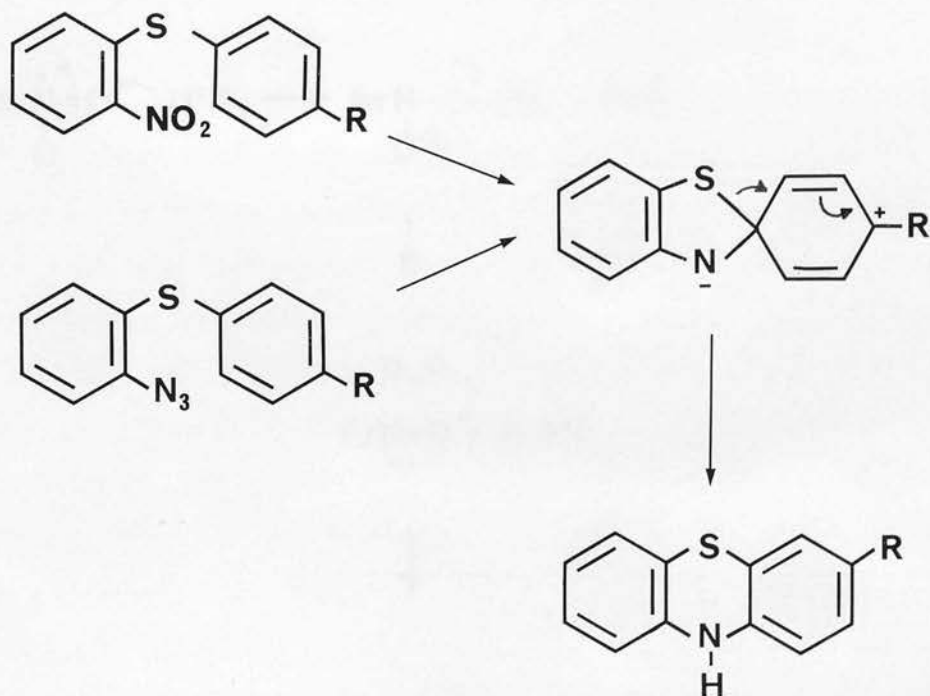
In the foregoing sections it has been assumed, for the most part, that reaction of tervalent phosphorus compounds with nitro- or nitroso-groups gives, initially, a nitrene, which then undergoes the reactions described. The principal support for this assumption is that the products obtained from the deoxygenation reactions are often very similar to those obtained from the thermolysis or photolysis of a corresponding azide. There is ample evidence,⁶⁹ including spectral data from frozen matrix techniques, to show that the azide decompositions proceed via nitrenes.

A simple example of this correspondence of products is that carbazole is formed in good yields from both the deoxygenation of 2-nitrobiphenyl by triethyl phosphite,¹ and the decomposition of 2-azidobiphenyl (154),⁶⁸ (Scheme 77).



Scheme 77

However, more impressive evidence for the common intermediacy of a nitrene comes from the examination of more complex systems, in which a similar correspondence of reaction products is frequently observed. For example, both the azide decompositions⁷⁰ and nitro/phosphite deoxygenations⁴⁹ give the same substituted phenothiazines from 2-azido- and 2-nitrophenyl aryl sulphides [section A. 2. (d)], and it was observed^{50a, c, 71} that the same rearrangement, possibly via a spiro-dienyl intermediate, occurs in each case (Scheme 78). Moreover, when meta-substituted azidobenzenes were

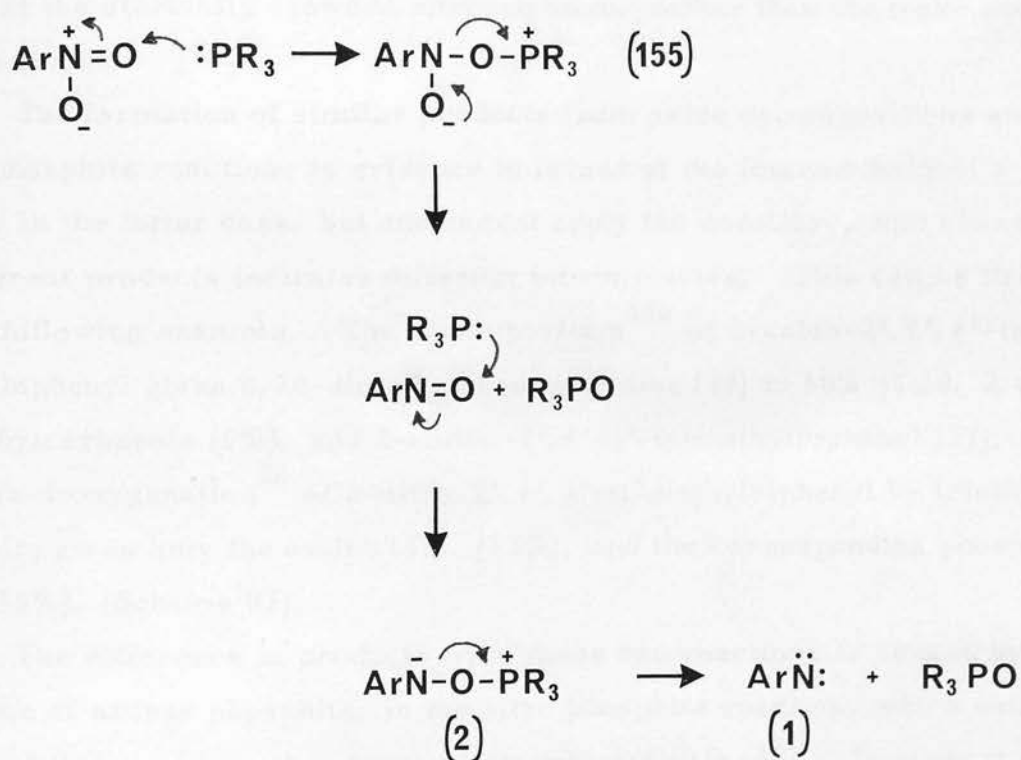


Scheme 78

photolysed²⁸ in the presence of diethylamine, the mixture of 4- and 6-substituted azepines was obtained in the same ratio as that which was obtained in the corresponding nitro/phosphite reaction,^{27, 28} described above [section A. 2. (a)].

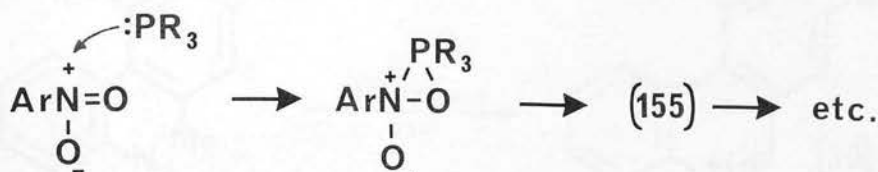
Although these reactions provide good evidence for a common intermediate, there are other cases where the diversity of products throws doubt on the intermediacy of a discrete nitrene (1) in the nitro/phosphite reaction. Before describing some examples in detail it is important to

consider the proposed mechanism for generation of the nitrene. Cadogan and his co-workers,^{26b, 72} having studied the reaction between 2-nitrobiphenyl and a range of tervalent phosphorus reagents, came to the conclusion that the rate determining step was nucleophilic attack by the phosphorus reagent at the nitro-group, leading to a dipolar species (155). Although direct evidence is lacking, this could then collapse to give the oxidised phosphorus reagent and a nitroso-group, which would undergo reaction with a further molecule of the phosphorus reagent to give a second dipolar species (2), and hence the nitrene (1) (Scheme 79).



Scheme 79

Although an alternative mechanism (Scheme 80), involving initial nucleophilic attack by the tervalent phosphorus reagent at the electron-deficient nitrogen, followed by rearrangement, appears to be a reasonable proposition, Sundberg and Lang⁷³ have provided evidence which shows that such a mechanism is unlikely, at least in the example studied. They compared the rates of deoxygenation of nitrobenzene and 2,4,6-trimethylnitrobenzene by triethyl phosphite, and found that the latter compound reacted only one hundred



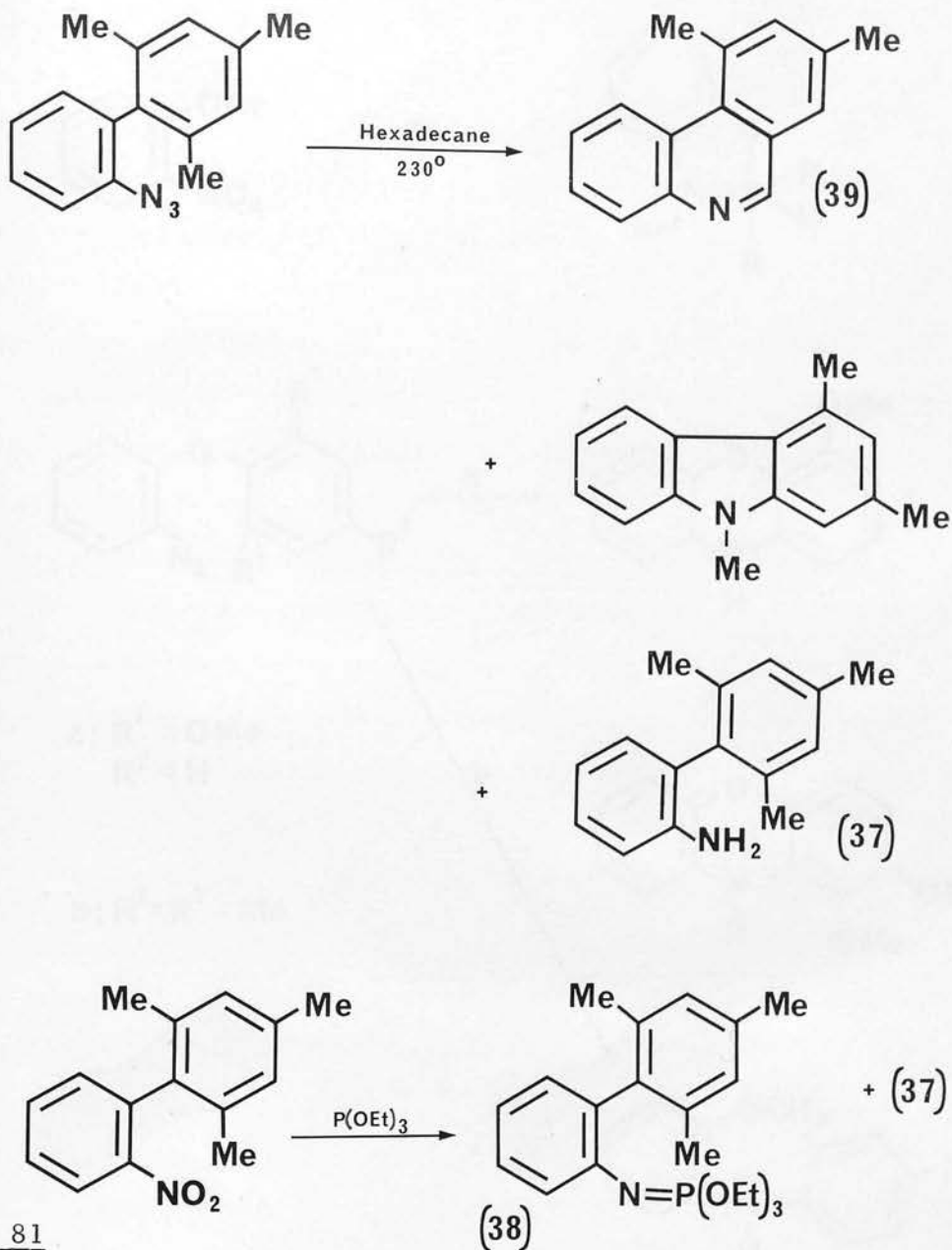
Scheme 80

times more slowly than nitrobenzene. Sundberg and Lang suggested that this figure should be much greater if the bulky phosphite molecule has to attack at the sterically crowded nitrogen atom, rather than the more accessible oxygen atoms.

The formation of similar products from azide decompositions and nitro/phosphite reactions is evidence in favour of the intermediacy of a nitrene in the latter case, but one cannot apply the corollary, that observation of different products indicates different intermediates. This can be illustrated by the following example. The decomposition^{69a} of 2-azido-2',4',6'-trimethylbiphenyl gives 8,10-dimethylphenanthridine (39) in 50% yield, 2,4,9-trimethylcarbazole (5%), and 2-amino-2',4',6'-trimethylbiphenyl (37), (30%), whereas deoxygenation²⁶ of 2-nitro-2',4',6'-trimethylbiphenyl by triethyl phosphite gives only the amine (37), (13%), and the corresponding phosphorimidate (38), (15%), (Scheme 81).

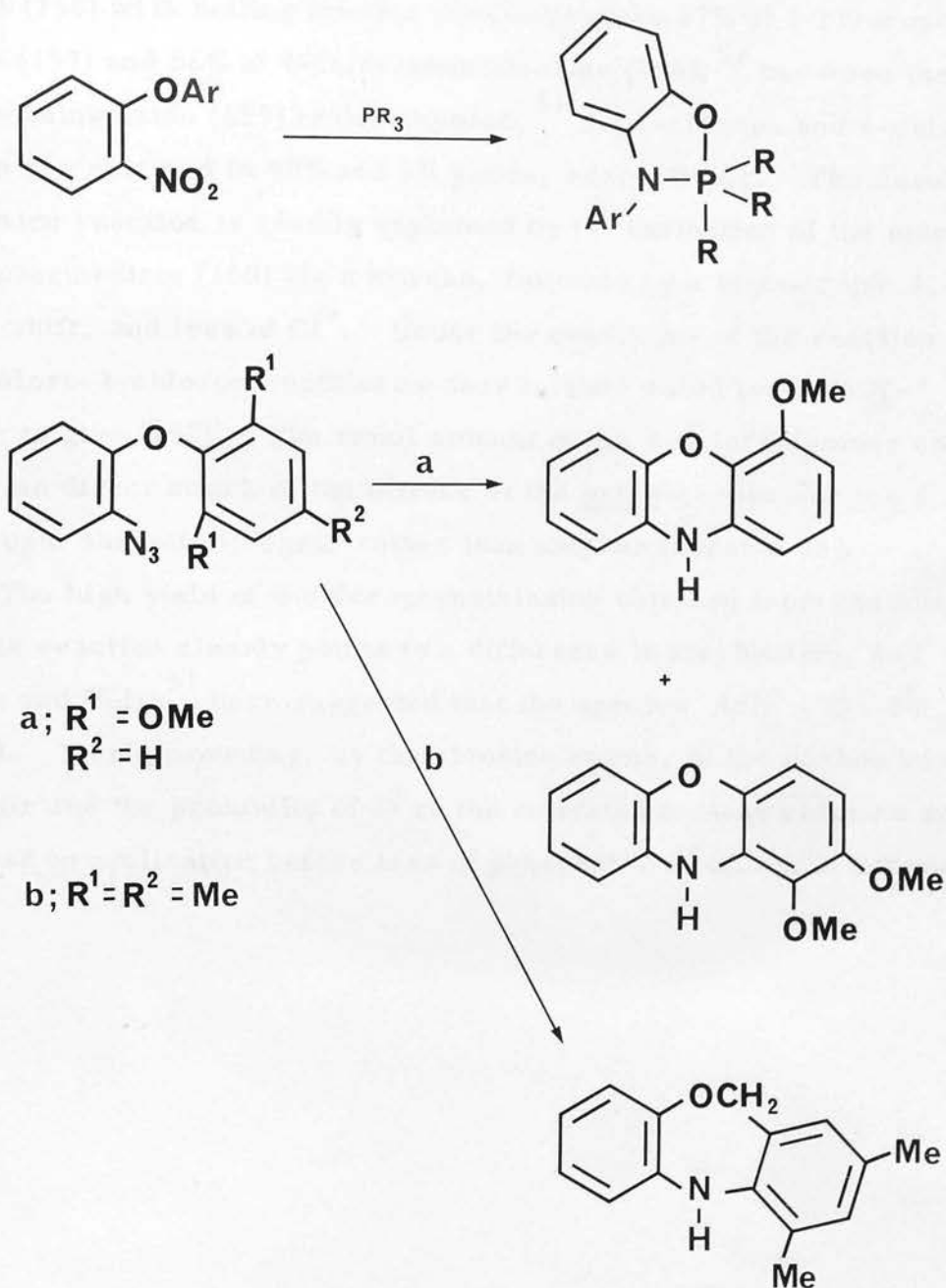
The difference in products from these two reactions is caused by the presence of excess phosphite, in the nitro/phosphite reaction, which can intercept the nitrene to give the observed phosphorimidate (38). In support of this argument, lowering the concentration of phosphite, by carrying out the reaction in *t*-butyl benzene, permits the formation of 8,10-dimethylphenanthridine in 12% yield.²⁶

Other examples in which decomposition of the azide and deoxygenation of the nitro-group give different results include 2-azido- and 2-nitrophenyl aryl sulphones, the former giving phenothiazine 5,5-dioxides,^{57,70} but the latter giving only tar. 2,6-Disubstituted aryl 2-nitro- and 2-azidophenyl



Scheme 81

ethers also give different products, and once again this is readily explained by the presence of excess phosphite in the nitro/phosphite reaction, rather than the lack of a common nitrene intermediate. As described above [section A. 2. (e)], the nitro-compounds⁵⁸ give benzoxazaphospholes by phosphite attack on an intermediate spirodiene, whereas the azides⁷⁵ give non-phosphorus-containing heterocycles (Scheme 82).



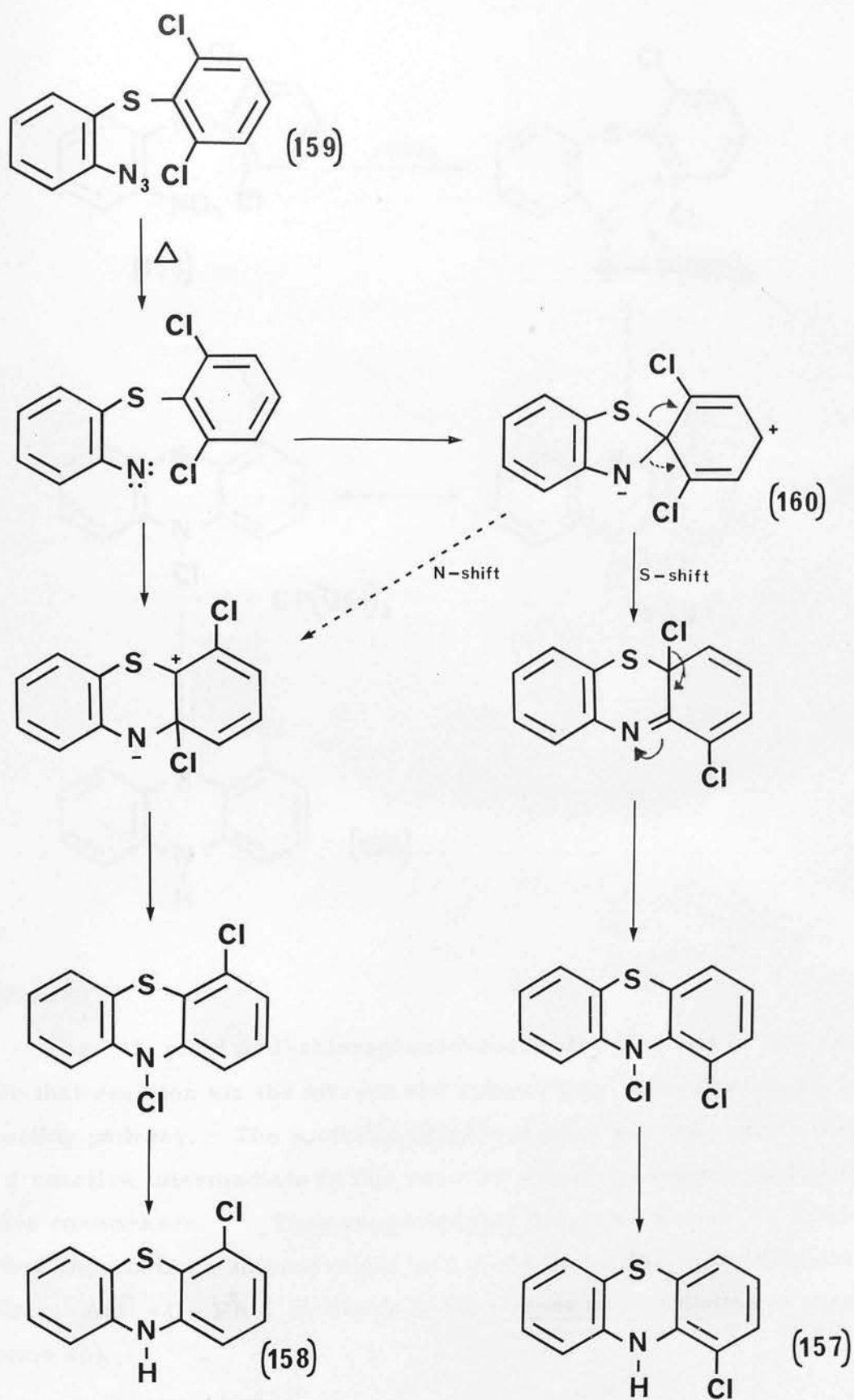
Scheme 82

In summary, these results provide little information to assist in deciding whether a discrete nitrene is involved in the nitro/phosphite reaction, or not.

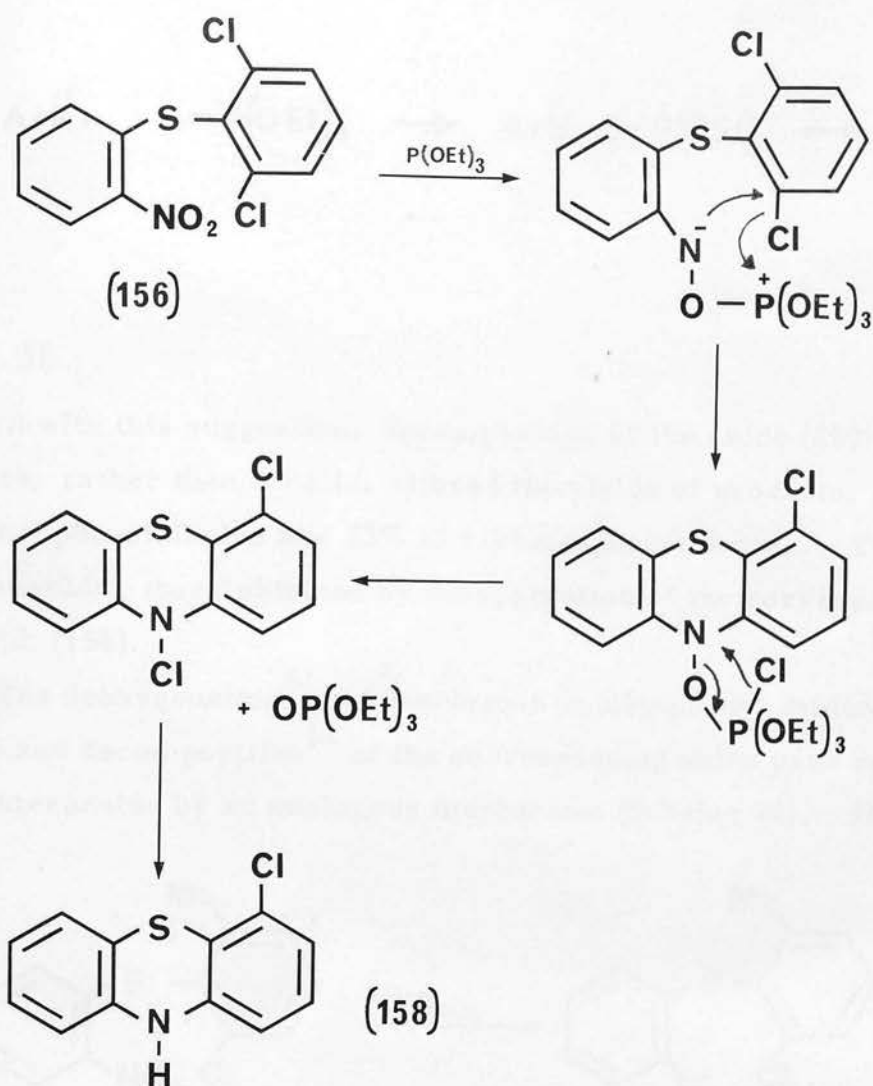
However, studies of 2,6-dichlorophenyl 2-nitrophenyl sulphide and 2-chloro-6-methylphenyl 2-nitrophenyl sulphide and the corresponding azides have provided quantitative results which require further consideration. As mentioned in section A. 2 (d), treatment of 2,6-dichlorophenyl 2-nitrophenyl

sulphide (156) with boiling triethyl phosphite gives 37% of 1-chlorophenothiazine (157) and 52% of 4-chlorophenothiazine (158),⁵¹ but when the corresponding azide (159) is decomposed,⁵¹ the 1-chloro- and 4-chloro-isomers are obtained in 40% and 5% yields, respectively. The result in the azide reaction is readily explained by the formation of the spirodienyl intermediate (160) via a nitrene, followed by a sigmatropic 1,2-sulphur shift, and loss of Cl^+ . Under the conditions of the reaction, the N-chloro-1-chlorophenothiazine thus formed would lose the N-chlorine to give (157). The small amount of the 4-chloro-isomer could arise from direct attack of the nitrene at the ortho-carbon, or via a 1,2-sigmatropic shift of nitrogen, rather than sulphur (Scheme 83).

The high yield of 4-chlorophenothiazine obtained from the nitro/phosphite reaction clearly points to a difference in mechanism, and Cadogan and Kulik⁵¹ have suggested that the species $\text{ArN}^- - \text{O} - \text{P}^+\text{R}_3$ is involved. Steric crowding, by the chlorine atoms, of the carbon bonded to sulphur and the proximity of P^+ to the activated nuclear chlorine atom could lead to cyclisation before loss of phosphate, as shown in Scheme 84.



Scheme 83



Scheme 84

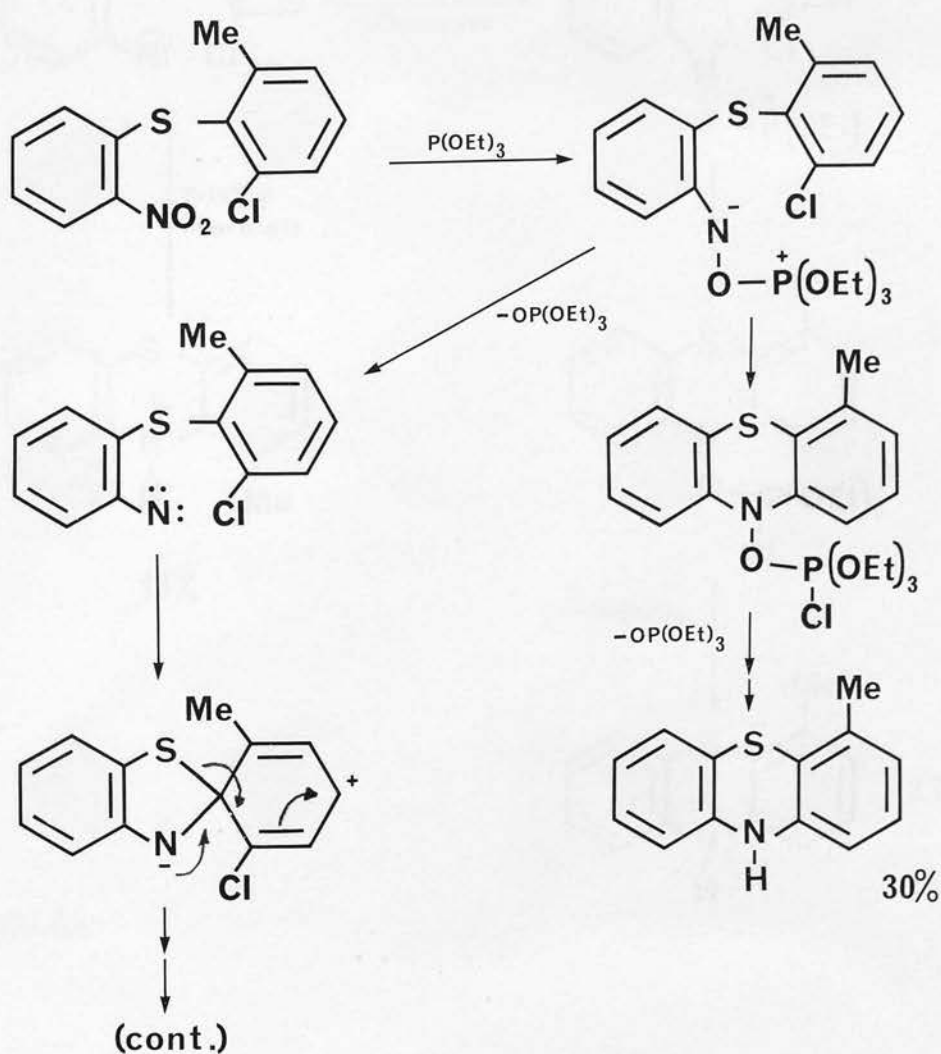
The 37% yield of 1-chlorophenothiazine also obtained in this reaction shows that reaction via the nitrene and spiro-diene, as in Scheme 83, is a competing pathway. The postulate that the dipolar species, $\text{Ar}\bar{\text{N}} - \text{O} - \text{P}^+\text{R}_3$, was a reactive intermediate in this reaction was given support by Holliman and his co-workers.⁷⁶ They suggested that decomposition of the azide in triethyl phosphate as solvent might lead to the formation of an identical intermediate, $\text{Ar}\bar{\text{N}} - \text{O} = \text{P}^+\text{R}_3$, by attack of the nitrene on a molecule of phosphate (Scheme 85).

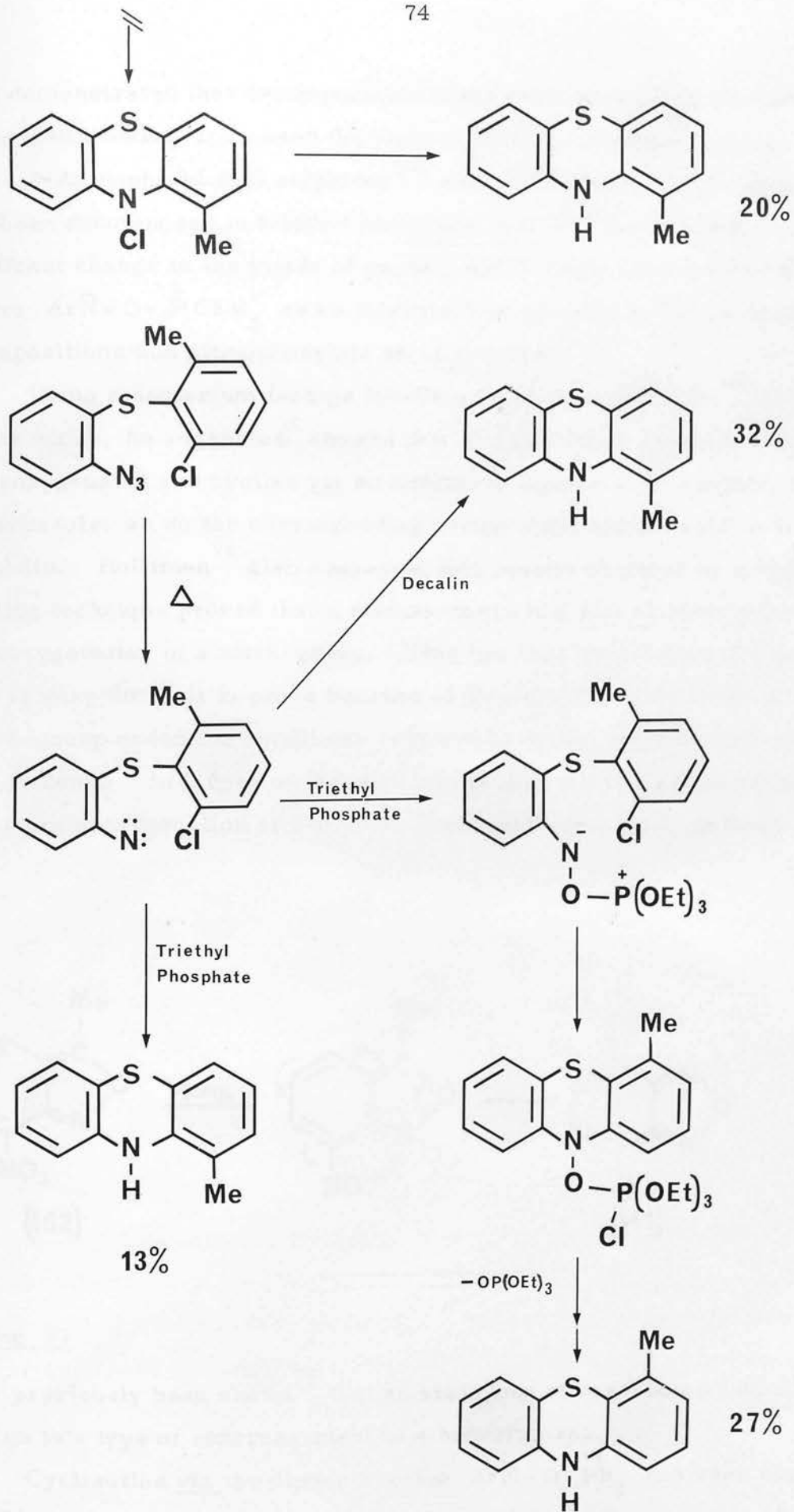


Scheme 85

In accord with this suggestion, decomposition of the azide (159) in triethyl phosphate, rather than decalin, altered the yields of products, giving 44% of 1-chlorophenothiazine and 23% of 4-chlorophenothiazine. These yields are approaching those obtained by deoxygenation of the corresponding nitro-compound (156).

The deoxygenation⁵¹ of 2-chloro-6-methylphenyl 2-nitrophenyl sulphide and decomposition⁵¹ of the corresponding azide gave results which can be interpreted by an analogous mechanism (Scheme 86). Holliman⁷⁶



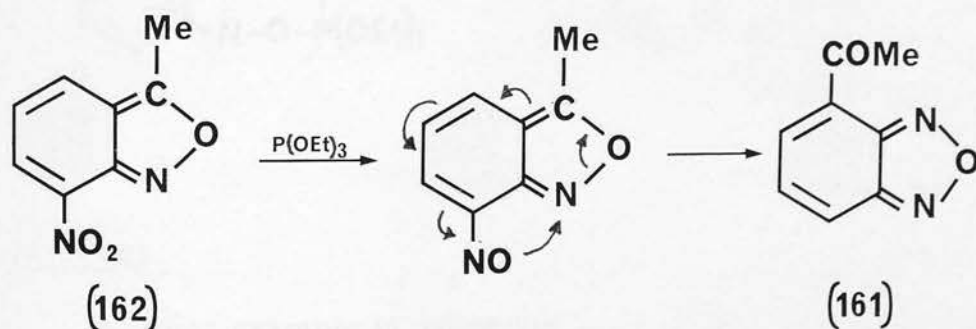


Scheme 86

again demonstrated that decomposition of the azide in triethyl phosphate rather than decalin, increased the yield of the 4-substituted isomer.

2-Azidophenyl aryl sulphides^{50d} and 2-azidophenyl aryl sulphones⁵⁷ have been decomposed in triethyl phosphate, but in these cases there is no significant change in the yields of product which might have implicated the species $\text{Ar}\ddot{\text{N}}-\text{O}-\overset{+}{\text{P}}(\text{OEt})_3$ as an intermediate common to the azide/phosphate decompositions and nitro/phosphite deoxygenations.

Using a deuterium isotope labelling technique, Holliman⁷⁶ obtained results which, he suggested, showed that 3'-substituted 2-nitrosobiphenyls are deoxygenated and cyclise via an analogous dipolar intermediate, to give the carbazole, as do the corresponding azides when decomposed in triethyl phosphate. Holliman⁷⁶ also suggested that results obtained by using his labelling technique proved that a nitroso-compound was an intermediate in the deoxygenation of a nitro-group. This has long been believed a possibility,³ but it is very difficult to prove because of the very high reactivity of the nitroso-group under the conditions required to deoxygenate a nitro-group.³ Good evidence⁷⁷ in favour of the postulate is the isolation of the benzofurazan (161) from deoxygenation of 3-methyl-7-nitroanthranil (162) (Scheme 87).

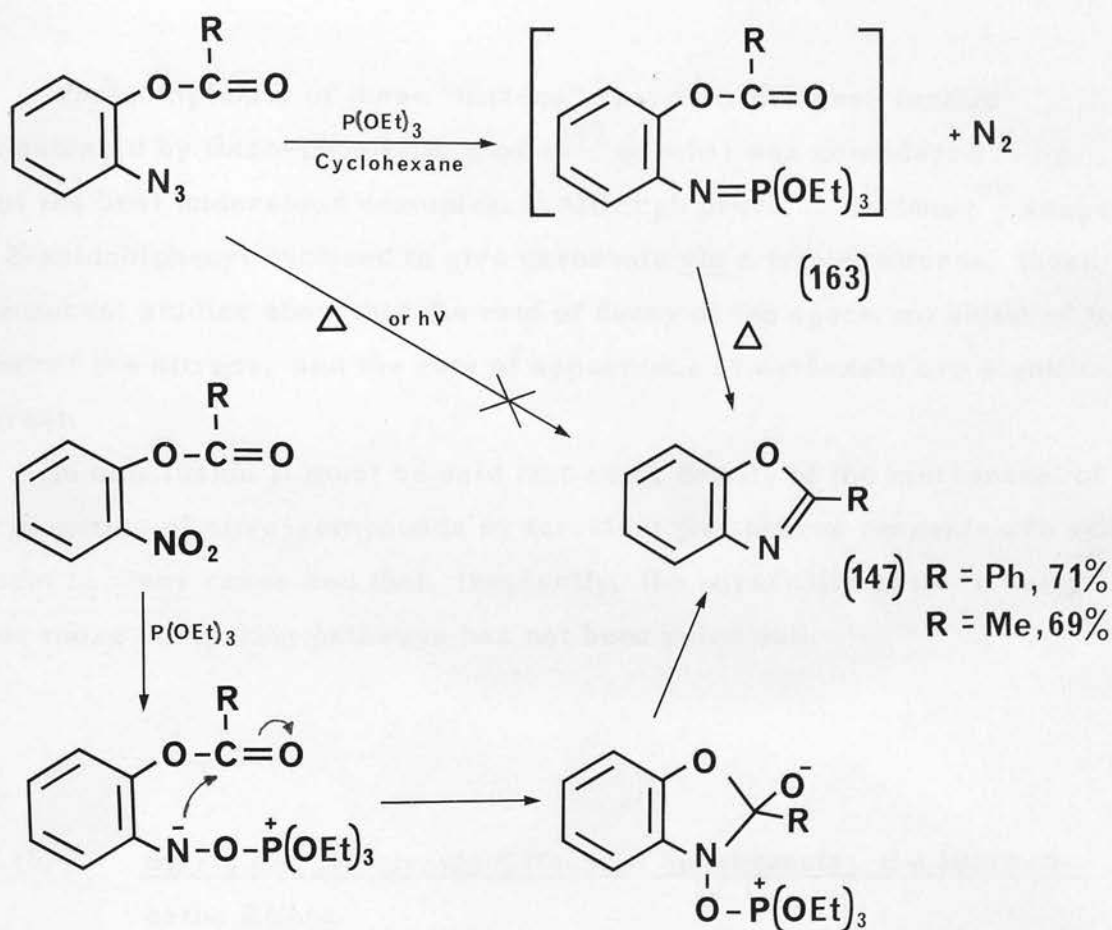


Scheme 87

It has previously been shown⁷⁸ that an analogous nitroso-compound does undergo this type of rearrangement to a benzofurazan.

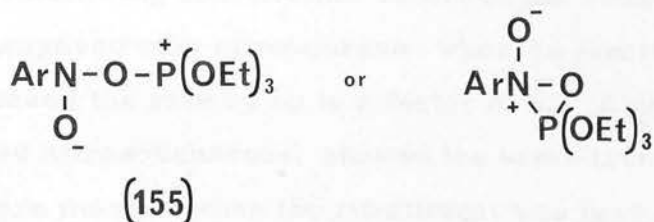
Cyclisation via the dipolar species $\text{Ar}\ddot{\text{N}}-\text{O}-\overset{+}{\text{P}}\text{R}_3$ has been suggested⁶³ to account for the formation of 2-methyl- and 2-phenylbenzoxazole (147) from

2-nitrophenylacetate and 2-nitrophenylbenzoate respectively. In these examples, thermolysis of the azide in cyclohexane alone gives no cyclised product, but in the presence of triethyl phosphite^{63b} high yields of the benzoxazoles are obtained, probably via the phosphorimide (163) (Scheme 88).



Scheme 88

Another example in which the intermediacy of a nitrene is challenged, is the formation of indoles by the deoxygenation of 2-nitrostyrenes. As described in section A. 2(c), Sundberg^{16a} provided good evidence that this reaction proceeds via the intermediacy of an N-hydroxylamine, which is presumably formed from the dipolar species (155), or its cyclic isomer, (see Scheme 32).



The complexity of these "nitrene" reactions has been further demonstrated by flash-photolytic studies⁷⁹ on what was considered to be one of the best understood examples. Although previous evidence⁸⁰ suggested that 2-azidobiphenyl cyclised to give carbazole via a triplet nitrene, these more recent studies show that the rate of decay of the spectrum believed to be that of the nitrene, and the rate of appearance of carbazole are significantly different.

In conclusion it must be said that exact details of the mechanism of deoxygenation of nitro-compounds by tervalent phosphorus reagents are still in doubt in many cases and that, frequently, the possibility of there being two or more competing pathways has not been ruled out.

A. 3. (b) Steric and Electronic Effects of Substituents: the Blocked-ortho Effect.

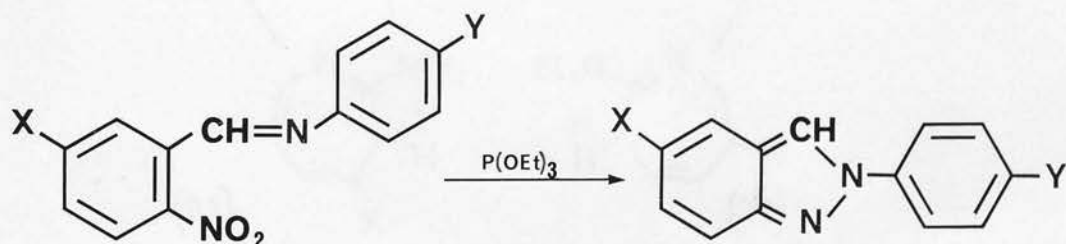
Studies of the classes of nitro-compounds discussed in section A. 2 have shown that their substituents can change both the rate of the reaction with tervalent phosphorus reagents, and the nature and distribution of the products.

Early kinetic experiments by Cadogan and Todd^{26b} showed that the rates of deoxygenation of 2-nitrobiphenyl and 4'-methyl-2-nitrobiphenyl were the same, but that the rate of deoxygenation of 4'-bromo-2-nitrobiphenyl was slightly greater. This suggested that deoxygenation, rather than subsequent ring closure, was the rate-determining step, and occurred via nucleophilic attack of phosphorus at the nitro-group.

A more detailed study of the rates of deoxygenation of mono-substituted

nitrobenzenes was published by Sundberg and Lang.⁷³ They also found that electron-withdrawing substituents enhanced the rate, by as much as a factor of 13, compared with nitrobenzene, whereas electron-releasing substituents decreased the rate by up to a factor of 6. A parallel study,⁷³ of mono-substituted nitrosobenzenes, showed the same trends. The effect on the rate was more marked when the substituent was para, rather than meta, to the nitro- or nitroso-group. Cadogan and his co-workers^{17b} also studied a range of substituted nitrobenzenes, but the emphasis was on the products of the reaction, [see section A. 2(a)], and these showed little sensitivity to the substituents.

A further thorough study⁷² of the effect of substituents on the rate of deoxygenation was made using o-nitrobenzylideneamines, which cyclise to give 2-arylidazoles (Scheme 89). The reactions were first-order in the

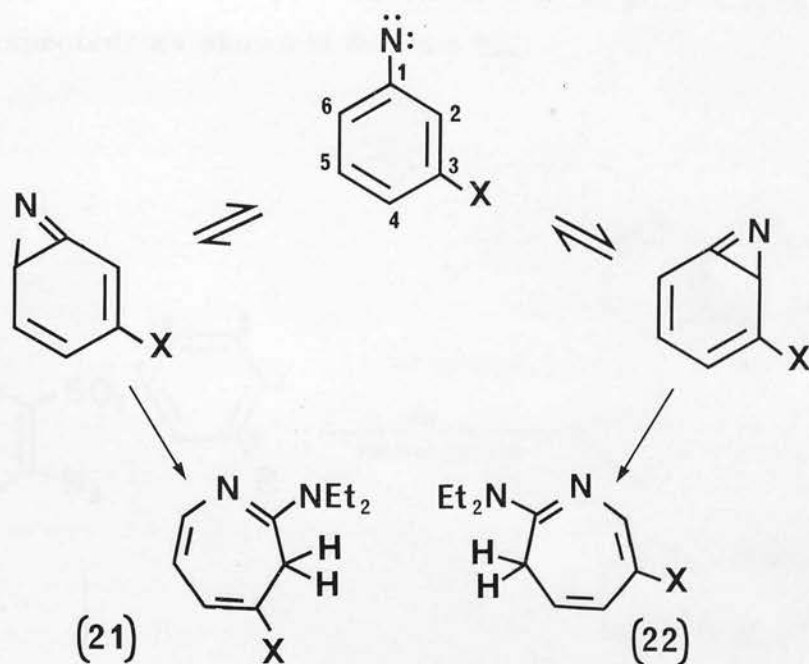


Scheme 89

nitro-compound, and alteration of substituent Y , (with $\text{X}=\text{H}$), had the expected effect on the rate, i.e. electron-withdrawing substituents increased the rate whereas electron-releasing substituents had the opposite effect. Although the trends are the same as those reported by Sundberg and Lang,⁷³ the magnitude of the effect is less, as indicated by the smaller Hammett ρ value obtained (0.75 for the o-nitrobenzylideneanilines⁷² compared to 1.75 for the nitrobenzenes⁷³). This is understandable in terms of the increased distance of the substituent Y from the reaction centre, compared with the substituents in the nitrobenzenes, as confirmed by the observation that substitution of X by Cl (see Scheme 89) had an effect on the rate 1.7 times greater than substitution of Y by Cl .

In addition to their effect on the rates of reaction, substituents may

alter the distribution of products. For example, as described in section A. 2(a), meta-substituted nitrobenzenes undergo deoxygenation in the presence of diethylamine²⁸ to give a mixture of 4- and 6-substituted 3H-azepines [(21) and (22) respectively] (Scheme 90). It was found that electron-withdrawing

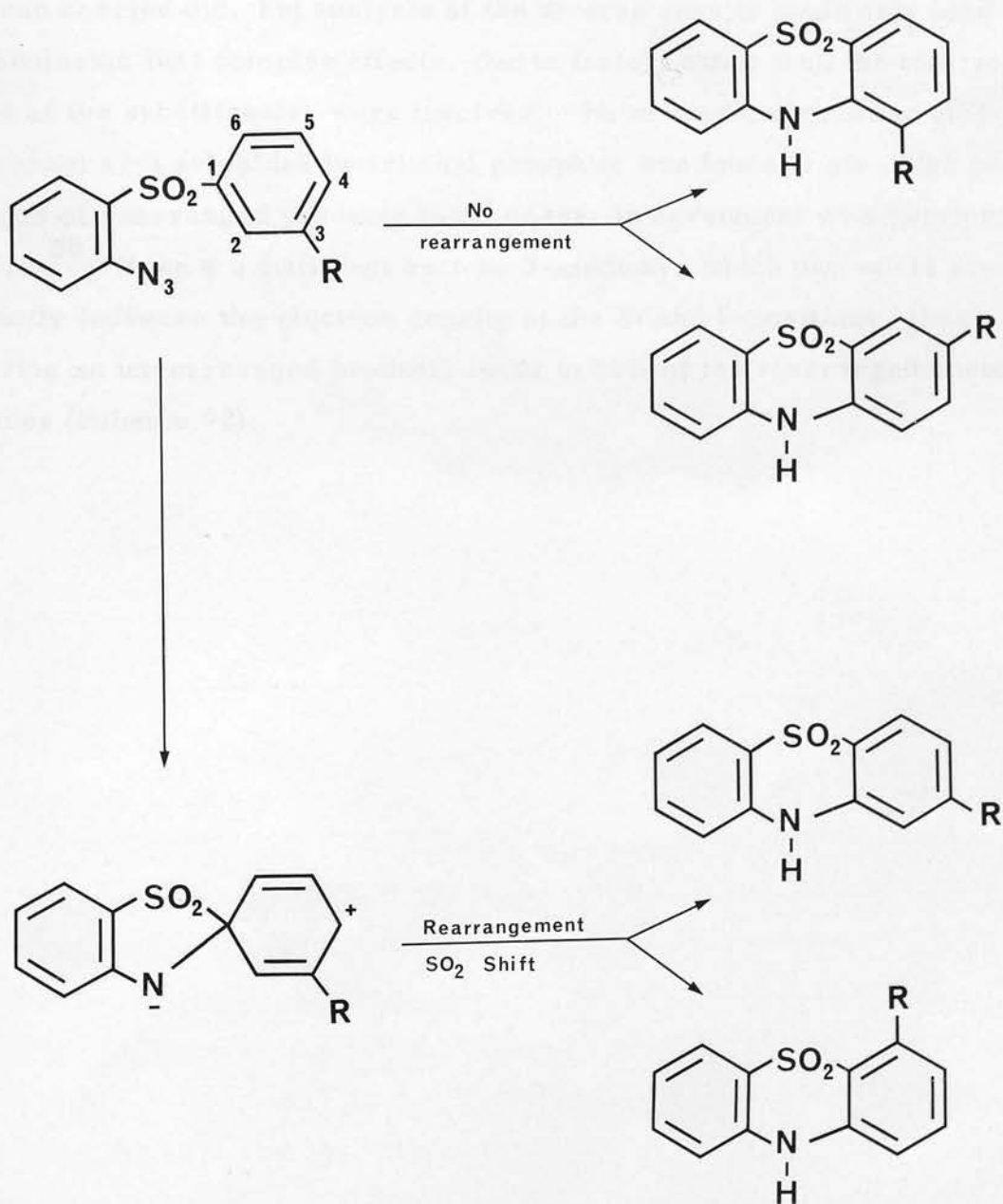


Scheme 90

substituents (X=Cl, Br, CO₂Et) increased the percentage of (22) by favouring cyclisation at the 2-position, whereas a strongly electron-releasing substituent (X=OMe) favoured cyclisation at the 6-position, to give (21). A meta-methyl group was indiscriminate in its effect on the equilibrium, and it would seem that in all cases the direction of the reaction is influenced by other factors in addition to the polarity of the substituents. para-Substituents did not greatly affect the yields of the one possible 3H-azepine,²⁸ except when the substituent was bromine, when the yield was reduced by 50%. No satisfactory explanation for this has been advanced, since experiments²⁸ have discounted a possible "heavy atom effect"⁸¹ of the bromine. With the exception of o-nitrotoluene, which gave 36% of 2-diethylamino-3-methyl-3H-azepine when deoxygenated by (EtO)₂PMe in diethylamine, o-substituted nitrobenzenes gave only unidentified tarry products,²⁸ possibly as a result of steric hindrance to some stage of the

reaction.

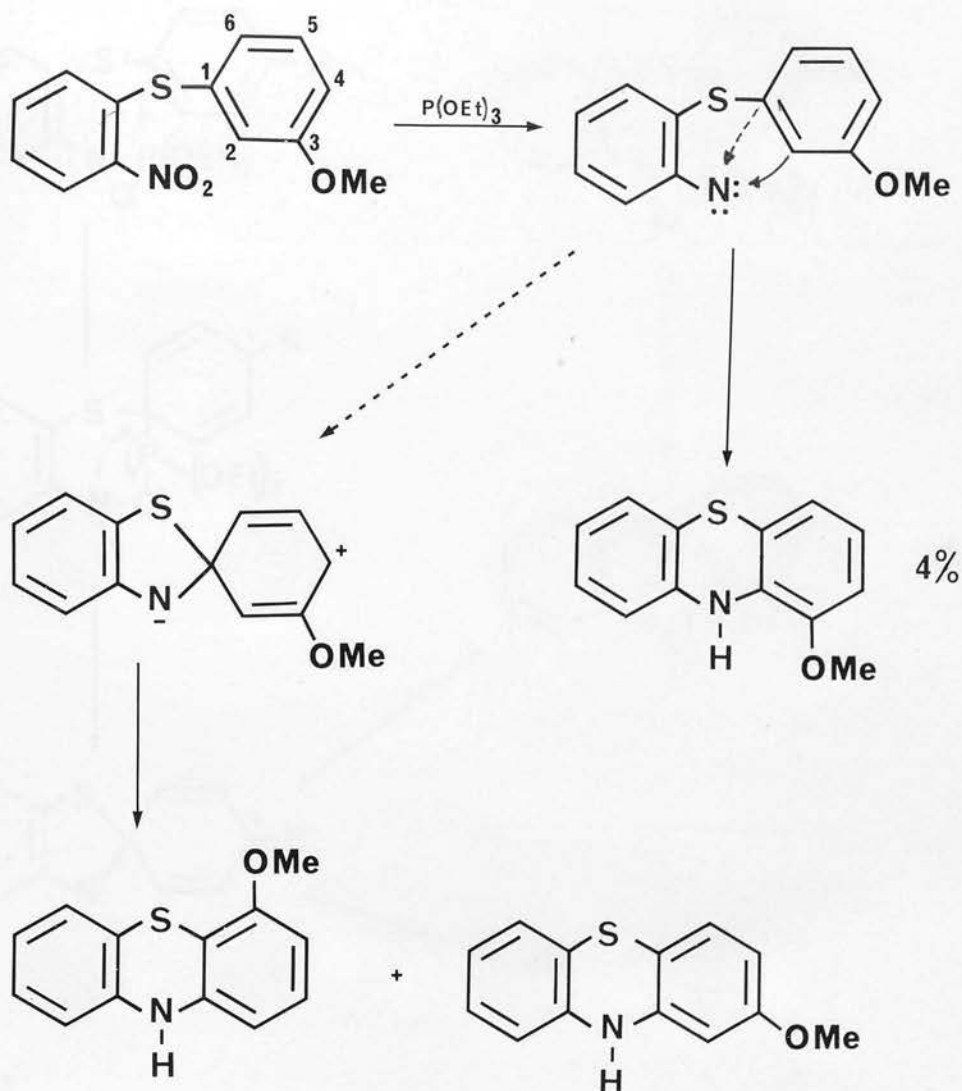
A study⁵⁷ of the thermal decomposition of 2-azidophenyl aryl sulphones showed that the ring closure of the nitrene, to give phenothiazine 5,5-dioxides, could proceed either with rearrangement, via a spiro-dienyl intermediate, or without rearrangement, by direct insertion into a C-H bond. With a substituent in the 3-position of the aryl ring, four possible products might be expected, as shown in Scheme 91.



Scheme 91

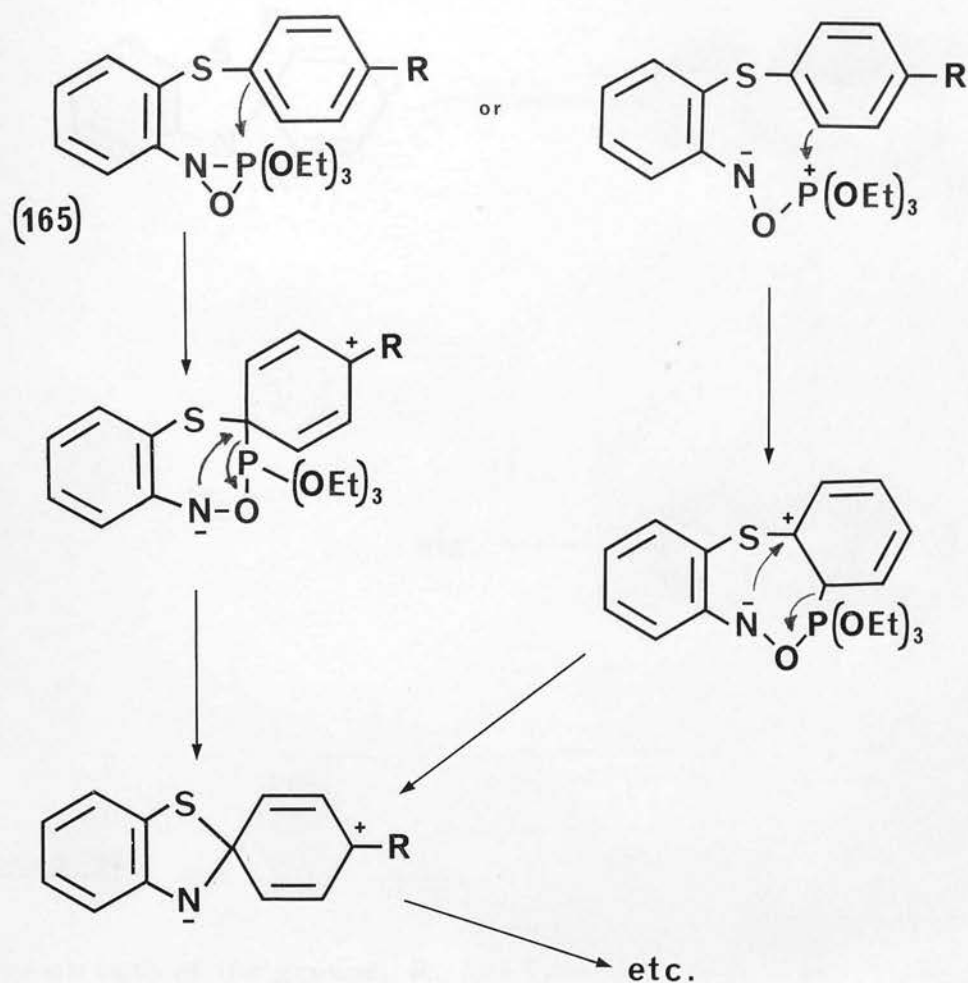
It was found that 3-substituents which direct ortho/para in electrophilic aromatic substitution reactions ($R=Me, MeO, Cl$) led to a higher percentage of unrearranged product, whereas a meta-directing group ($R=CF_3$) gave more rearranged products. Similar results were obtained for 2-azidophenyl 4-substituted aryl sulphones, but 2-substituents, including $-CF_3$, gave predominantly rearranged products. This could be a steric or statistical effect, rather than an electronic effect, because of there being only the single 2-position available for direct insertion.

A similar study^{50d} of the corresponding 2-azidophenyl aryl sulphides has been carried out, but analysis of the diverse results could only lead to the conclusion that complex effects, due to factors other than the electronic nature of the substituents, were involved. However deoxygenation of 2-nitrophenyl aryl sulphides by triethyl phosphite was found to give high percentages of rearranged products in all cases, in agreement with previous reports.⁵⁰ Even a substituent such as 3-methoxy, which one would expect to greatly increase the electron density at the 2- and 6-positions, thus favouring an unrearranged product, leads to 96% of the rearranged phenothiazines (Scheme 92).



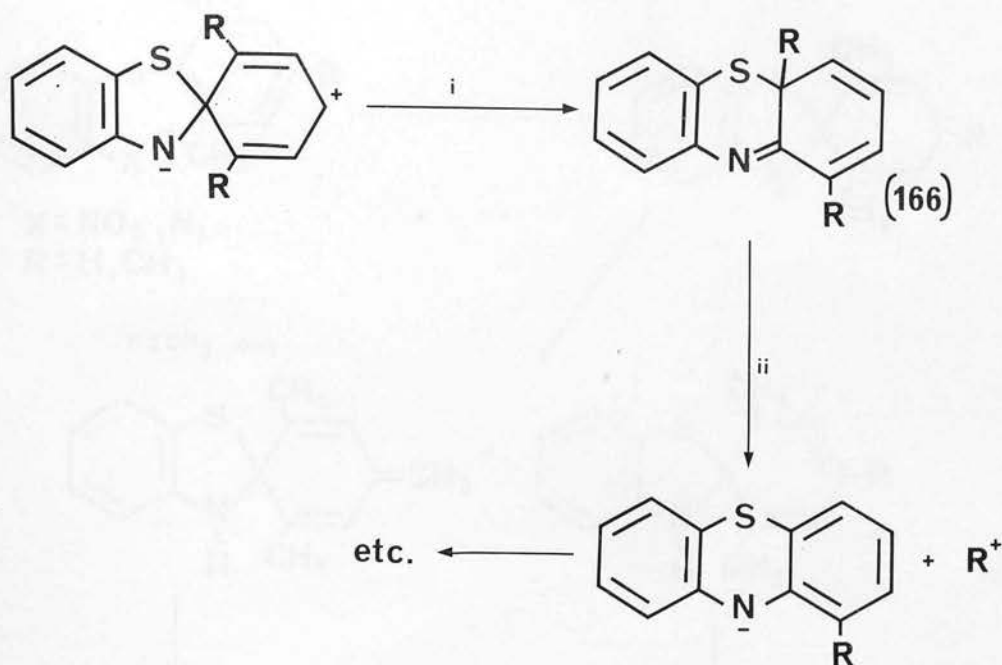
Scheme 92

It has been argued^{50d} that this absence of any large electronic effect indicates that powerful steric factors are favouring ring closure at the carbon bonded to sulphur (the 1-position), thus giving the five-membered ring of the spiro-dienyl intermediate. Since the corresponding azide decompositions give different results, it has been suggested that ring closure occurs via initial electrophilic attack by the bulky P^+ species (165) at the 1- or 2-position of the aryl ring (Scheme 93).



Scheme 93

The rearrangement which occurs during the formation of phenothiazines, discussed in section A. 2(d), (Scheme 55), involves two steps which could be influenced by ortho-substituents, (i) the 1, 2-sulphur shift and, (ii) rearomatization, (Scheme 94).

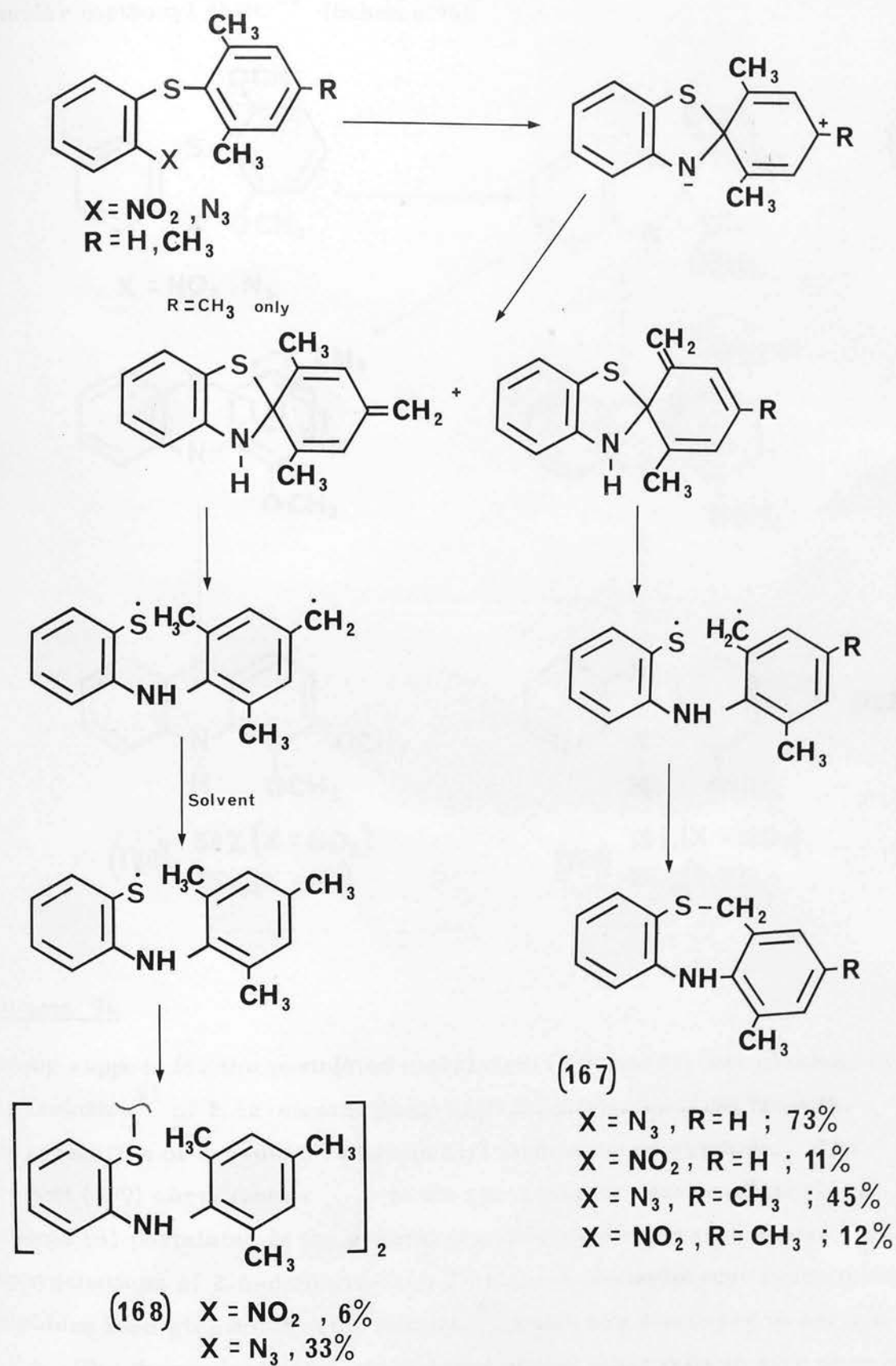


Scheme 94

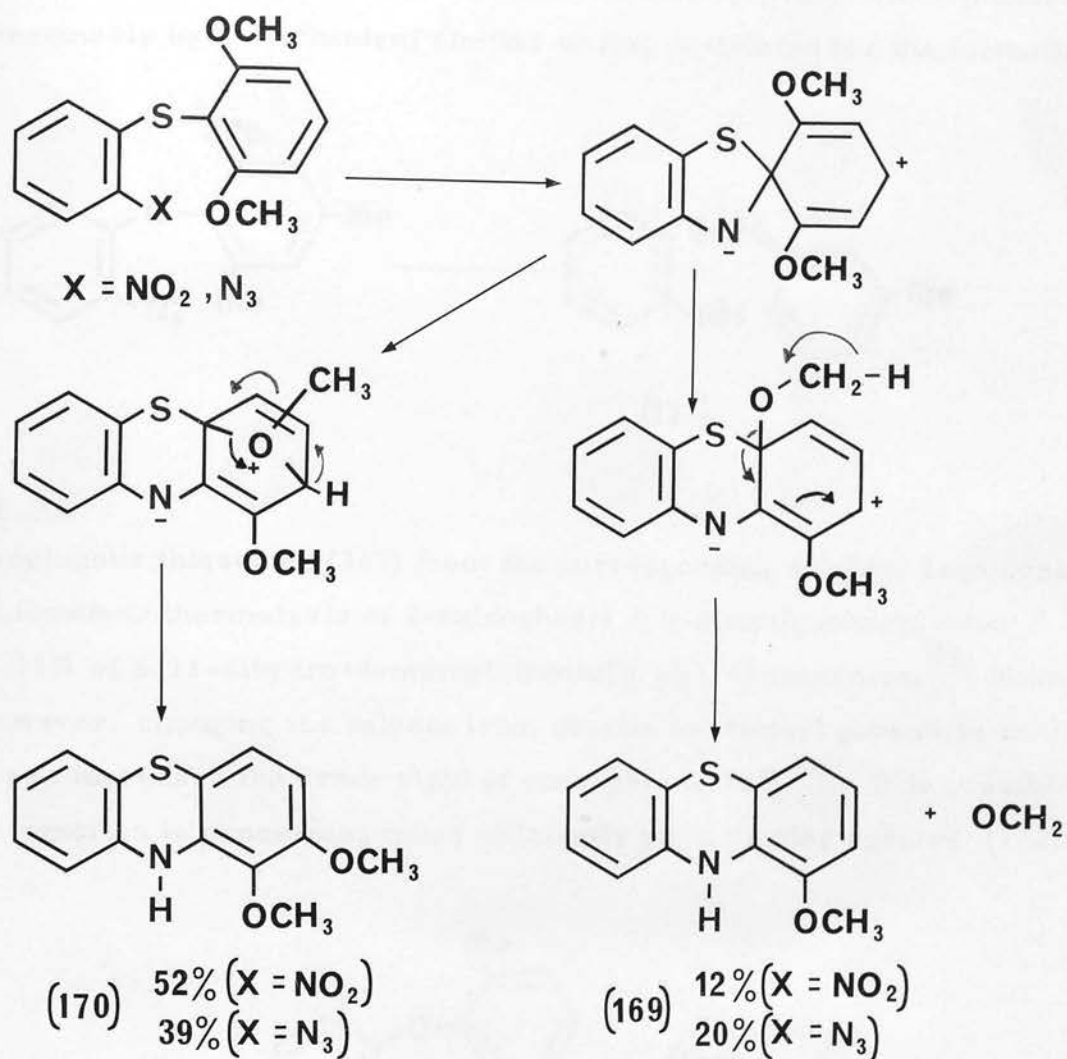
If one or both of the groups, R, are hydrogen, then there is little impedence to either of these steps, but if the substituents are groups other than hydrogen, step (i) may be affected by steric hindrance, and step (ii) by the migratory aptitude of the groups, R. In several cases the result has been to give unexpected products, and has been called the "blocked-ortho" effect.⁵

In the case of 2,6-dimethyl- and 2,4,6-trimethylphenyl 2-nitro (or 2-azido)phenyl sulphide, the main result of the blocked-ortho effect is the formation of a 5,11-dihydro-dibenzo[b,e][1,4]-thiazepine derivative (167),⁵¹ (Scheme 95). The radical mechanism proposed by Cadogan and Kulik⁵¹ also explains the formation of the disulphide (168) from the trimethyl-substituted sulphide, as shown in Scheme 95.

2-Nitro(or 2-azido)phenyl 2,6-dimethoxyphenyl sulphide does react to give two phenothiazine derivatives, but the route to one of these (169) results in loss of formaldehyde, and the second route, to (170), involves a trans-



annular methoxyl shift,⁵¹ (Scheme 96).

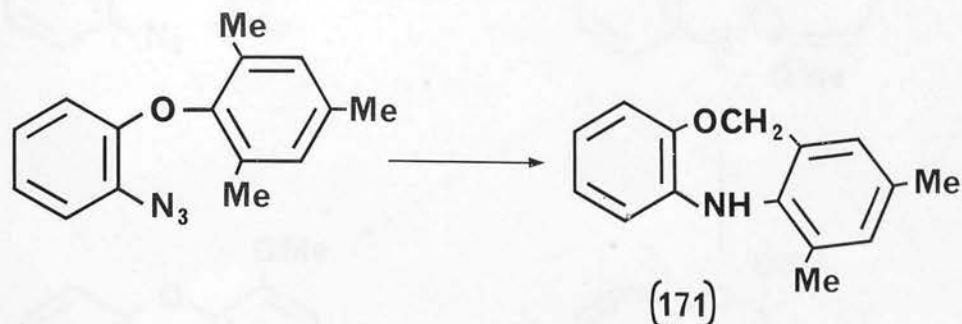


Scheme 96

Strong support for the postulated mechanism (Scheme 94) was obtained by the isolation⁵¹ of 1,4a-dicarbethoxy-4aH-phenothiazine (109) from the deoxygenation of 2,6-dicarbethoxyphenyl 2-nitrophenyl sulphide. The product (109) corresponds to the non-aromatic intermediate (166; Scheme 94) postulated in the general phenothiazine rearrangements. The deoxygenations of 2,6-dichloro- and 2-chloro-6-methylphenyl 2-nitrophenyl sulphides also give noteworthy results,⁵¹ which are discussed in section A. 3(a).

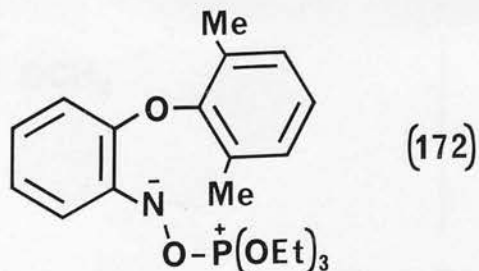
The thermolysis of 2-azidophenyl phenyl ether fails to give phenoxazine,⁷⁰ but application of the blocked-ortho effect can lead to products analogous to those obtained from the corresponding sulphides. In this way 5,11-dihydro-

2,4-dimethyldibenzo[b, e][1,4]oxazepine (171) was obtained in 15% yield⁷⁵ from the thermolysis of 2-azidophenyl 2,4,6-trimethylphenyl ether (Scheme 97), presumably by a mechanism similar to that postulated for the formation



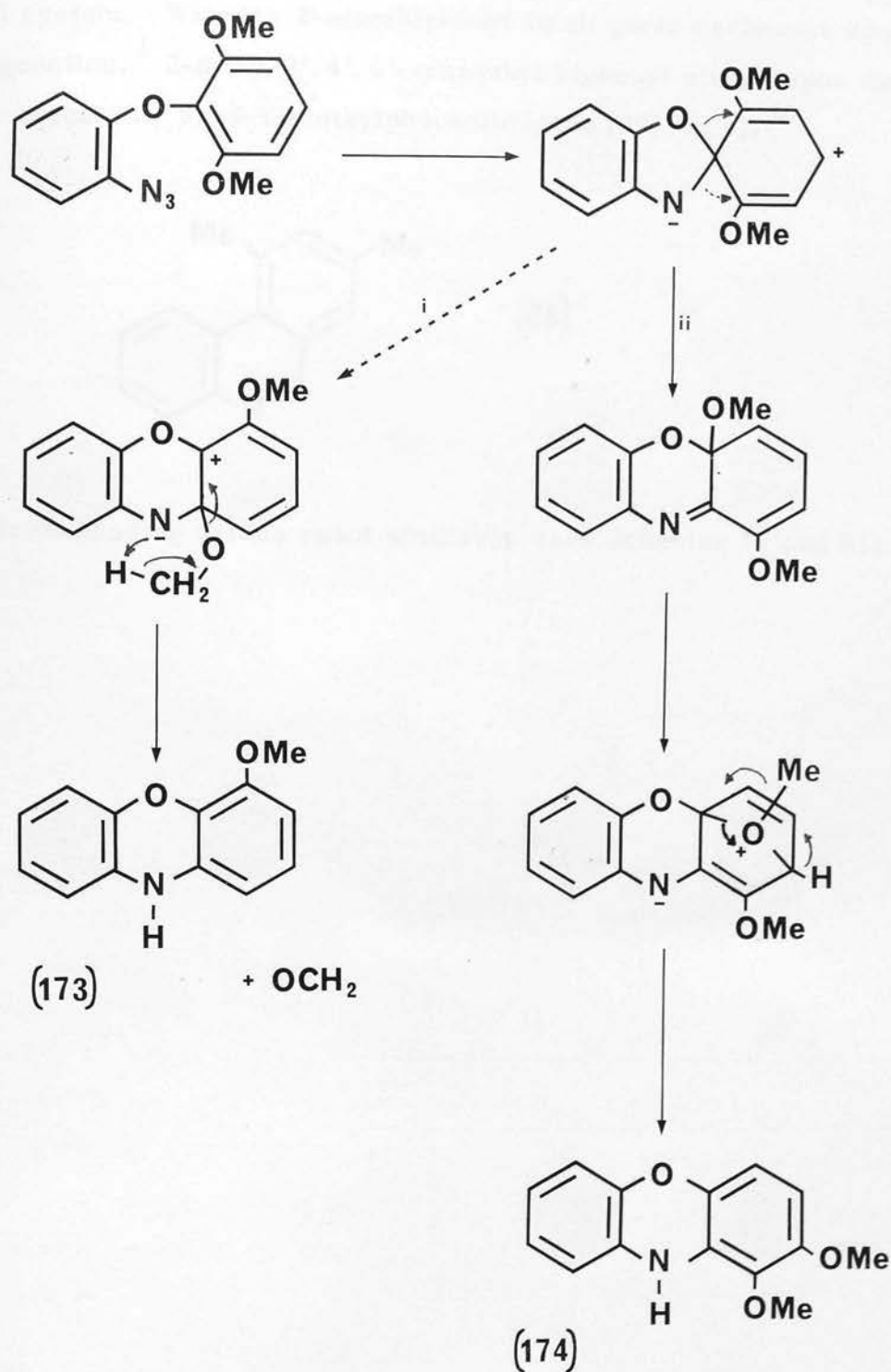
Scheme 97

of the analogous thiazepine (167) from the corresponding sulphide (see Scheme 95). Likewise, thermolysis of 2-azidophenyl 2,6-dimethylphenyl ether affords 11% of 5,11-dihydro-4-methyldibenzo[b, e][1,4]oxazepine.⁷⁵ Interestingly however, changing the solvent from decalin to triethyl phosphate in this latter case increases the crude yield of oxazepine to 73%.⁸² It is possible that the reaction is proceeding more efficiently via a dipolar species (172),



but it is not easy to confirm this, because deoxygenation of 2,6-dimethylphenyl 2-nitrophenyl ether which might be expected to proceed via the same intermediate, gives only 3% of the oxazepine,⁵⁸ most of the material reacting with excess phosphite to give the benzoxazaphosph(v)ole, as described in sections A. 2(e) and B. 2.

By a mechanism similar to the formation of methoxyphenothiazines from the corresponding sulphide (see Scheme 96), thermolysis of 2,6-dimethoxyphenyl 2-azidophenyl ether gives 4-methoxyphenoxazine (173) (35%) and 1,2-dimethoxyphenoxazine (174) (15%),⁷⁵ (Scheme 98). However, the migratory aptitude of oxygen is less than that of sulphur, with the result that a 1,2-nitrogen shift is competitive [path (i); Scheme 98] and the 4-methoxy isomer

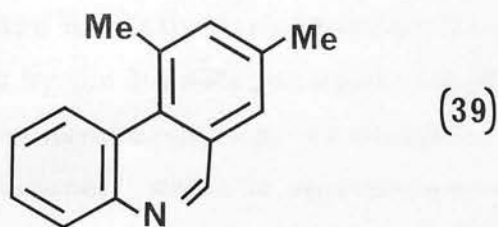


Scheme 98

(173) is produced, in contrast to the formation of 1-methoxyphenothiazine (169) from the analogous sulphide (see Scheme 96). The two methoxyphenoxazines, (173) and (174), were obtained in 5% and 2% yields respectively from the deoxygenation of 2,6-dimethoxyphenyl 2-nitrophenyl ether.^{58a}

Finally, a blocked-ortho effect has been observed in the 2-nitrobi-

phenyl system. Whereas 2-nitrobiphenyl itself gives carbazole upon deoxygenation,¹ 2-nitro-2',4',6'-trimethyl biphenyl gives, upon deoxygenation in a solvent, 8,10-dimethylphenanthridene (39) (12%).²⁶



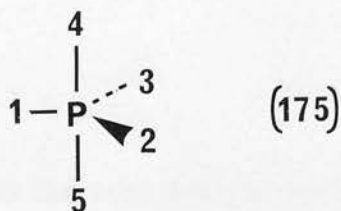
The corresponding azides react similarly (see Schemes 77 and 81).

B. Pentacoordinated Phosph(v)oles

B.1 General considerations; Structure and Preparation.

The phosphorus compounds to be discussed in this section of the introduction are formally derivatives of the pentahydride of phosphorus, PH_5 , as designated by the P oxidation state, (v), and all include the phosphorus atom in a five-membered ring, as designated by the suffix "-ole." The term "phosphorane," which is applicable to all P(v) species, is also frequently used to describe compounds of this type. The five-membered ring may include other heteroatoms in addition to phosphorus.

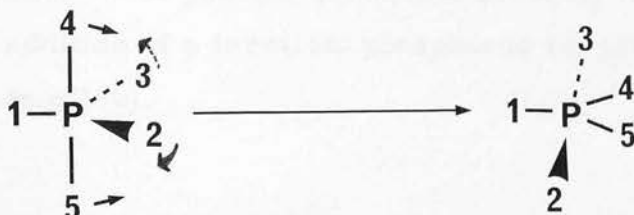
The preferred geometrical arrangement of five ligands about a central phosphorus atom is usually trigonal bipyramidal (175),^{83, 84} with the result



that three equatorial ligands (1, 2 and 3) are in a different environment from the two axial ligands (4 and 5). However the axial and equatorial ligands are interchangeable by a process which does not involve the breaking of bonds, so that, although one might expect to observe two signals in the n. m. r. spectrum, corresponding to the two sets of ligands, this is commonly seen only at low temperatures, when the interchange process is sufficiently slow, or "frozen."⁸⁵

This type of ligand interchange has been called Regular Permutational Isomerisation, and two mechanisms, Berry Pseudorotation,⁸⁶ and Turnstile Rotation,⁸⁷ have been proposed. There appears to be a continuing discussion⁸⁸ over which mechanism best describes the process, but the details are of greater theoretical than practical significance, so the less complex Berry Pseudorotation will be employed throughout this thesis. The mechanism effectively exchanges pairs of axial and equatorial ligands in a concerted

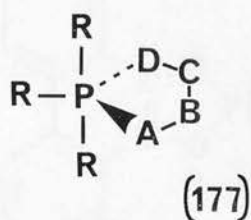
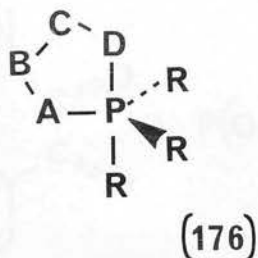
process, while the third equatorial ligand, called the pivot, remains stationary. Referring to Scheme 99, the pivot ligand (1) remains stationary as axial ligands (4 and 5) move away from the pivot, in the plane of the page, while the equatorial ligands (2 and 3) move apart, towards the pivot, in a plane perpendicular to the page. At one point during this process the ligands assume a square pyramidal geometry, the high energy point of the process. Repetition of the process, taking each ligand in turn as pivot, permits a total geometrical equivalence of the ligands to be achieved.



Scheme 99

However the nature of the substituents themselves can result in some permutations of the ligands having lower energies than others. In general, ligands bound to phosphorus through atoms having higher electronegativity have greater affinity for an axial position than those bonded through carbon.^{87b, 89} Affinity for the axial position is called the apicophilicity of a ligand, and is connected with the difference in the two sets of hybridised (sp^3d) molecular orbitals of the phosphorus atom, axial and equatorial, and the molecular orbitals of the ligands themselves. The possible extent of back-bonding between available electrons on the ligand and low-lying empty d -orbitals in the phosphorus ($pd-\pi$ bonding), is also an influencing factor.

A further constraint is applied to the pseudorotation when a pair of ligands are linked to form a ring. This is particularly true of the phosph(v)oles, because the five-membered ring readily accommodates the 90° angle formed between axial and equatorial ligands, but is put under considerable strain when forced into a di-equatorial configuration. This leads to the much greater stability of (176) than (177), especially if A or D, or both, are heteroatoms.^{89b}

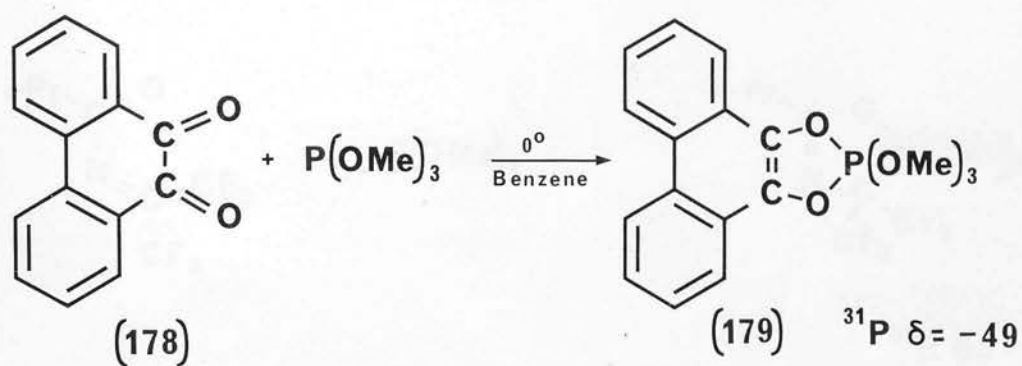


A survey of the literature shows that several types of reaction lead to the formation of phosph(v)oles, but probably the most general method has been the addition of a tervalent phosphorus reagent to a 1,3-unsaturated system (Scheme 100).

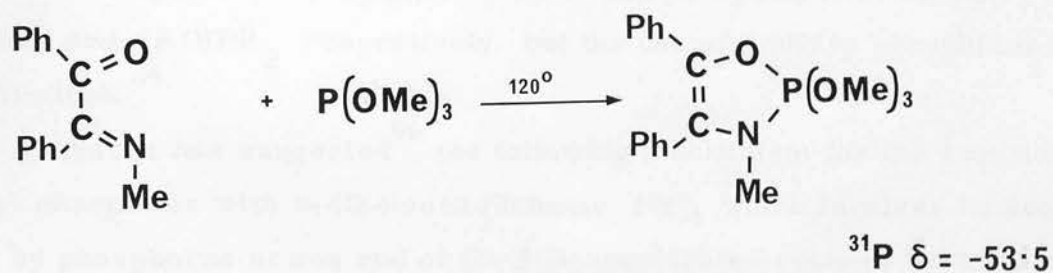


Scheme 100

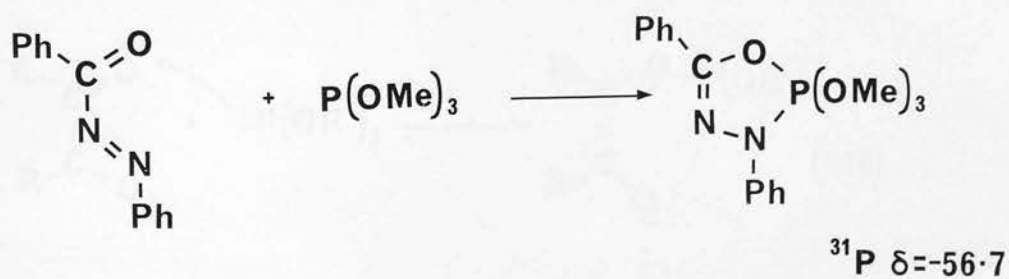
For example 9,10-phenanthraquinone (178) reacts with trimethyl phosphite⁹⁰ to give a 1:1 adduct (179) (Scheme 101), and X-ray analysis⁹¹ of the tri-isopropyl analogue of this oxyphosphorane provided substantial geometrical data to support some of the generalisations described above. In addition to α -dicarbonyl compounds, which react to give 1,3,2-dioxaphos(v)ole derivatives such as (179), β -ketoimines react to give 1,3,2-oxazaphos(v)ole derivatives (e.g. Scheme 102),⁹² β -keto-azo-compounds give 1,3,4,2-oxadiazaphos(v)oles (e.g. Scheme 103),⁹³ and α,β -unsaturated ketones give 1,2-oxaphos(v)oles (e.g. Scheme 104),⁹⁴ or 1,3,5-oxazaphos(v)oles (e.g. Scheme 105).⁹⁵



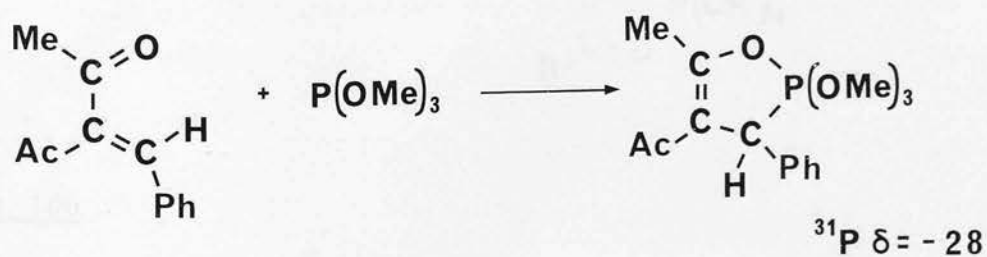
Scheme 101



Scheme 102



Scheme 103



Scheme 104

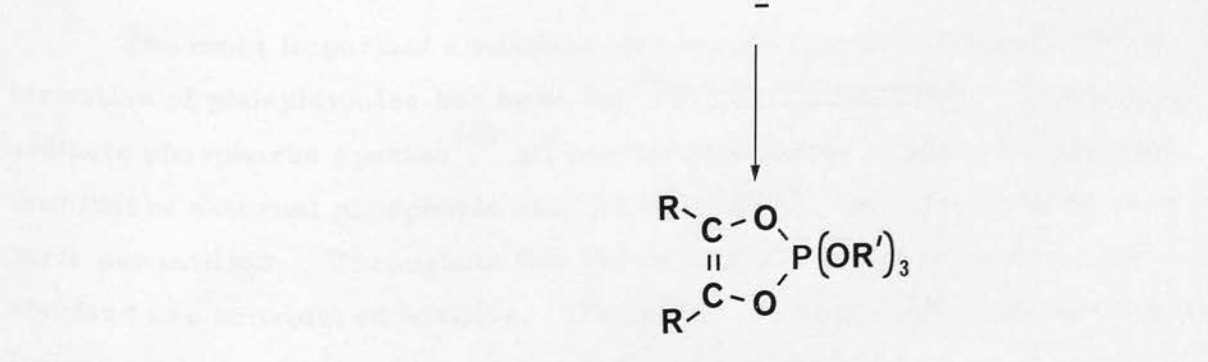


P 0 = -35.5

Scheme 105

Analogous phosphoranes can usually be prepared using other trivalent phosphorus reagents, including phosphonite and phosphinite esters. 87a

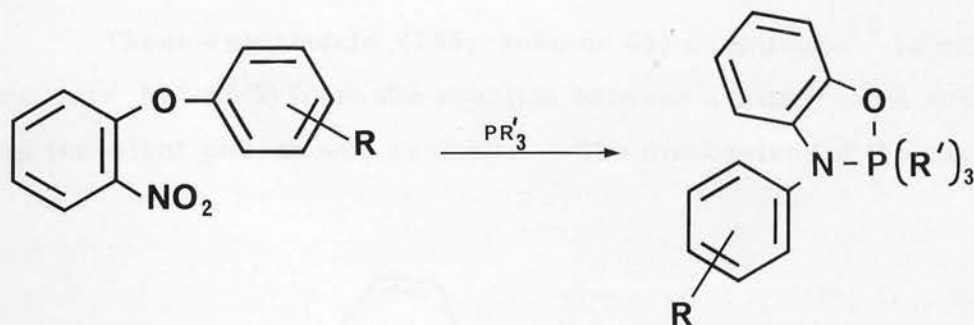
Ramirez has suggested⁹⁶ the following mechanism for the reaction of trialkyl phosphites with α -diketones (Scheme 106), which involves nucleophilic



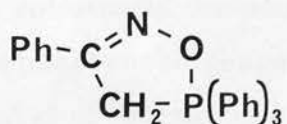
Scheme 106

not unlikely that a similar mechanism operates in the other examples quoted (Schemes 102-105).

Other preparations of phosph(v)oles include the reduction, by trivalent phosphorus reagents, of 2-nitrophenyl phenyl ethers⁵⁸ (Scheme 107), discussed in section B. 2, and the reaction of phosphorus ylides with 1, 3-dipoles^{98, 99} (e. g. Scheme 108), discussed in section B. 3.



Scheme 107



$^{31}\text{P} \delta = -37$

Scheme 108

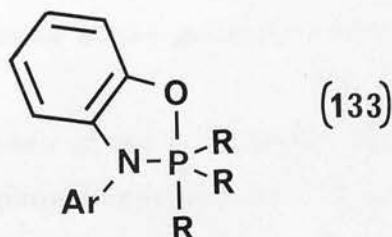
The most important analytical tool for the identification and characterisation of phosph(v)oles has been the ^{31}P n.m.r. spectrum. Pentacoordinate phosphorus species¹⁰⁰ all exhibit resonances to lower frequencies than that of external phosphoric acid (H_3PO_4 , 85%), which is taken as zero parts per million. Throughout this thesis shifts to high frequency of the standard are considered positive. The shifts (δ) of phosph(v)oles are negative, typical examples having been shown in the schemes above.

B. 2 Benzoxaza- and Benzothiazaphosph(v)oles Formed by Reduction of 2-Nitrodiaryl-ethers and -sulphides with Tervalent Phosphorus Reagents.

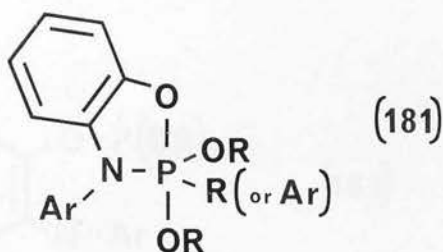
B. 2 (a) Preparation and Structure

(i) 3-Aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles.

These compounds (133; scheme 66) were found⁵⁸ to be the major products (12-95%) from the reaction between 2-nitrophenyl aryl ethers and tervalent phosphorus reagents. The mechanism of the reaction,



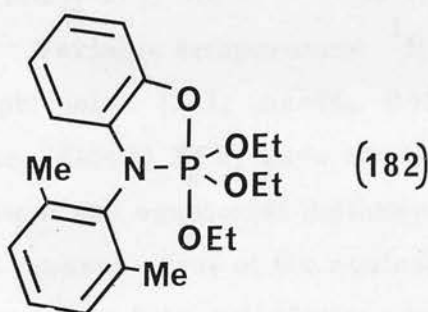
proposed by Cadogan and his co-workers,⁵⁸ is described in section A. 2(e). The general method of preparation involves boiling a solution of the nitro-compound with four mole-equivalents of the tervalent phosphorus reagent in dry cumene, under nitrogen, for 65 hours. Removal of the solvent and excess of the phosphorus reagent, under reduced pressure, is followed by careful high-vacuum distillation to give the 1,3,2-benzoxazaphosph(v)ole (133) as a solid, or as an oil. Exclusion of water at all times is essential because of the sensitivity of the product to hydrolysis. Tait^{58, 82} found that most phosphorus reagents gave high yields of relatively pure 1,3,2-benzoxazaphosph(v)oles (133) when they reacted with 2,6-disubstituted phenyl 2-nitrophenyl ethers, so long as the substituents were not too bulky. However, when the reaction was extended to ethers without ortho-blocking groups better results were obtained by using phosphonites, $(RO)_2PR'$ or $(RO)_2PAr$, rather than phosphites, $(RO)_3P$. The stability of the resulting phosph(v)ole (181) is increased, relative to the corresponding trialkoxy-compound, because the alkyl or aryl group is accommodated in



an equatorial position more readily than an apicophilic alkoxy-group.

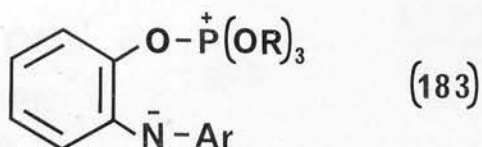
The structure of the 1,3,2-benzoxazaphosph(v)oles (133) was determined by examination of the hydrolysis products⁵⁸ and by analytical and spectroscopic techniques.¹⁰¹ X-Ray crystallographic studies¹⁰² confirmed several details of the geometry which had been suggested by the spectral data.

The mass spectra of the compounds showed the loss of a fragment corresponding to the phosphorus moiety. For example, 3-(2,6-dimethyl-phenyl)-2,3-dihydro-2,2,2-triethoxy-1,3,2-benzoxazaphosph(v)ole (182)



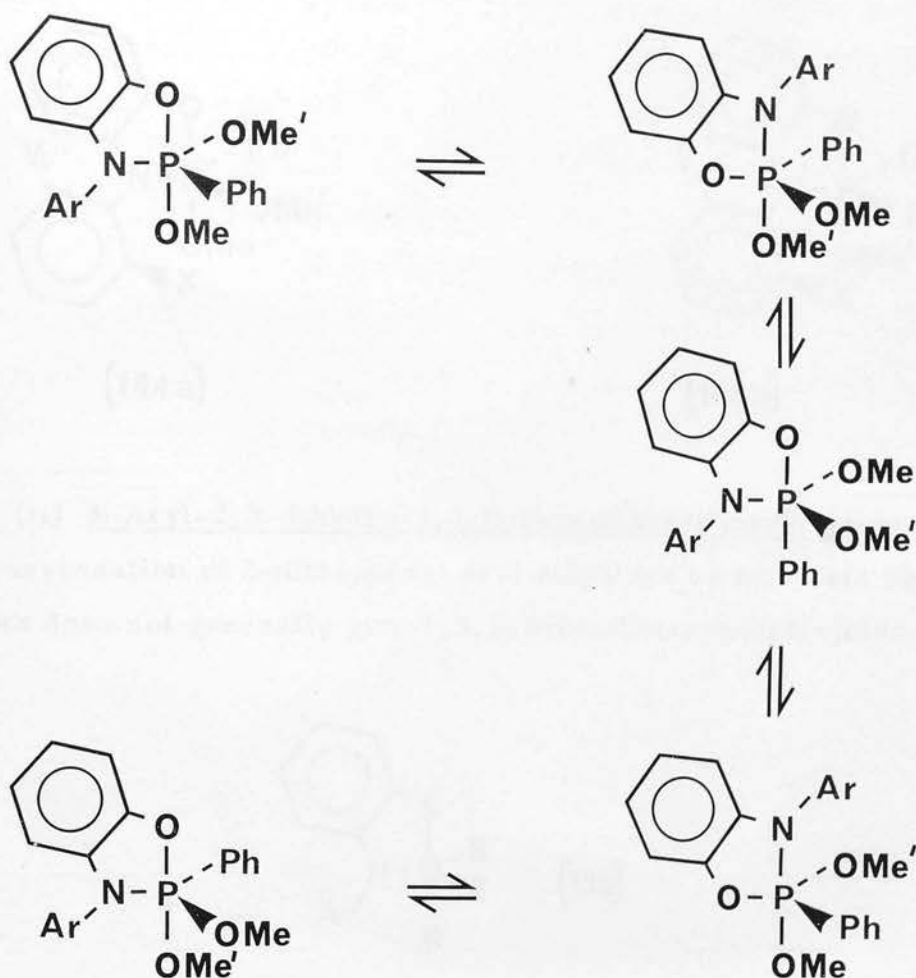
lost the fragment $(\text{EtO})_3\text{POH}$, and it was also observed that loss of ethylene, by McLafferty rearrangement, occurred.^{58a}

³¹P n.m.r. spectra showed characteristic signals in the range -33.3 to -62 p. p. m., which excluded the possibility of an open-chain zwitterionic form (183), which would have a positive shift. The possibility of an equilibrium between the open and ring-closed tautomers was discounted by the observation that the spectra recorded with CDCl_3 - $(\text{CF}_3)_2\text{CH.OH}$ as solvent showed only a very small downfield shift



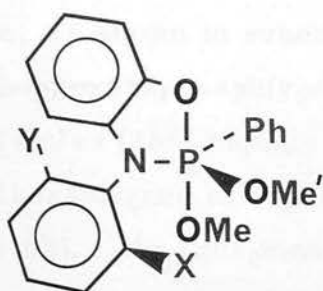
(< 6 p. p. m.), whereas authentic examples involving this type of tautomerism give shifts of up to 87 p. p. m.^{87a}

¹H n. m. r. data shows that one proton of the benzoxazaphosph(v)ole system is considerably shielded, giving an absorption signal at δ ca 5.9 (relative to internal T.M.S.). This suggests that the N-aryl group is orthogonal to the benzoxazaphosph(v)ole nucleus, and that there is restricted rotation about the N-aryl bond.¹⁰¹ This has been confirmed by the X-ray studies.¹⁰² Variable temperature ¹H n.m.r. studies¹⁰¹ of the 1,3,2-benzoxazaphosph(v)oles (181; Ar=Ph, R=Me) derived from dimethylphenylphosphonite, (MeO)₂PPh, have shown that, at sufficiently low temperatures, the apical and equatorial methoxy-groups may be separately observed, and measurement of the coalescence temperature of these two signals has permitted the calculation of the free energy of activation, ΔG^* , for the two-site exchange process outlined in scheme 109.¹⁰¹

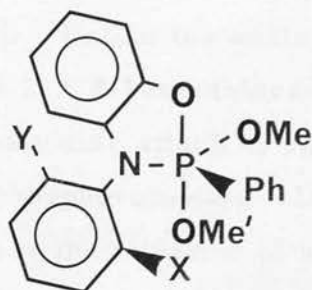


Scheme 109

Each of the three intermediate configurations shown in Scheme 109 has one ligand, either the phenyl or amino-group, in an unfavourable apical position, resulting in an energy barrier to the interchange of the methoxy-ligands. Another effect arising from the pentaco-ordinate phosph(v)ole structure, which involves substituents on the N-aryl ring, has been observed in certain cases.¹⁰¹ This is the direct observation by n. m. r. of pairs of unequally populated diastereoisomeric forms (184a) and (184b).¹⁰³ Diastereoisomers may arise, when $X \neq Y$, because of asymmetry introduced by restricted rotation about the N-aryl bond.



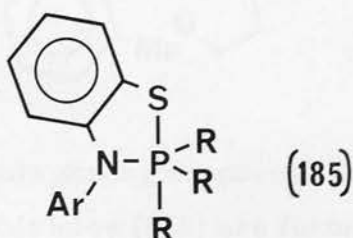
(184a)



(184b)

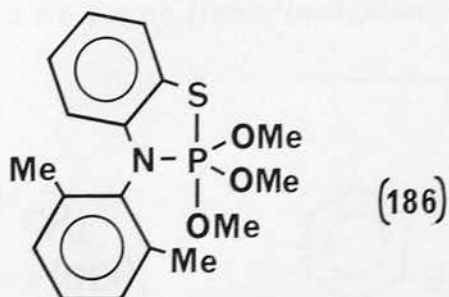
(ii) 3-Aryl-2,3-dihydro-1,3,2-benzothiazaphosph(v)oles.

The deoxygenation of 2-nitrophenyl aryl sulphides by trivalent phosphorus reagents does not generally give 1,3,2-benzothiazaphosph(v)oles (185)



(185)

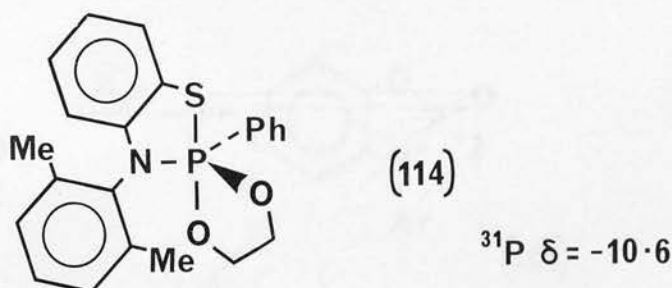
which can be isolated, but, instead, good yields of non-phosphorus-containing heterocyclic compounds.⁵⁰ However, examination of the deoxygenation of 2,6-dimethylphenyl 2-nitrophenyl sulphide by ^{31}P n. m. r. spectroscopy, showed that a transitory species having a chemical shift of -23.98 p. p. m., and thought to be the phosph(v)ole (186), was produced.



(186)

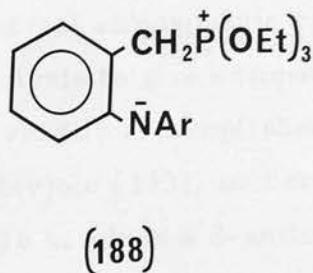
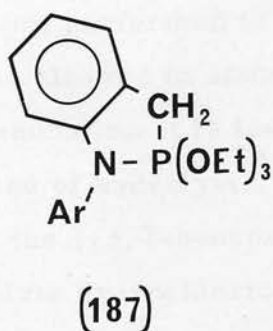
It was suggested by Cadogan and Tait⁵² that, in the case of ortho-blocked 2-nitrophenyl aryl sulphides, formation of a benzothiazaphosph(v)ole (185)

could compete with the generally more facile rearrangement to a phenothiazine, as shown in scheme 58 [section A. 2(d)]. Unlike the analogous 1,3,2-benzoxazaphosph(v)oles (133) however, the 1,3,2-benzothiazaphosph(v)oles (185) rapidly decompose by intramolecular attack of sulphur at an alkoxy-ligand of the phosphorus, to give a phosphoramidate (110; scheme 58). An exception to this generalisation is the isolation of a stable spiro-benzothiazaphosph(v)ole (114),⁵³ which is obtained in 73% yield when the deoxygenating agent is 2-phenyl-1,3,2-dioxaphospholan (115; scheme 59). The structure of compound (114) has been confirmed by X-ray



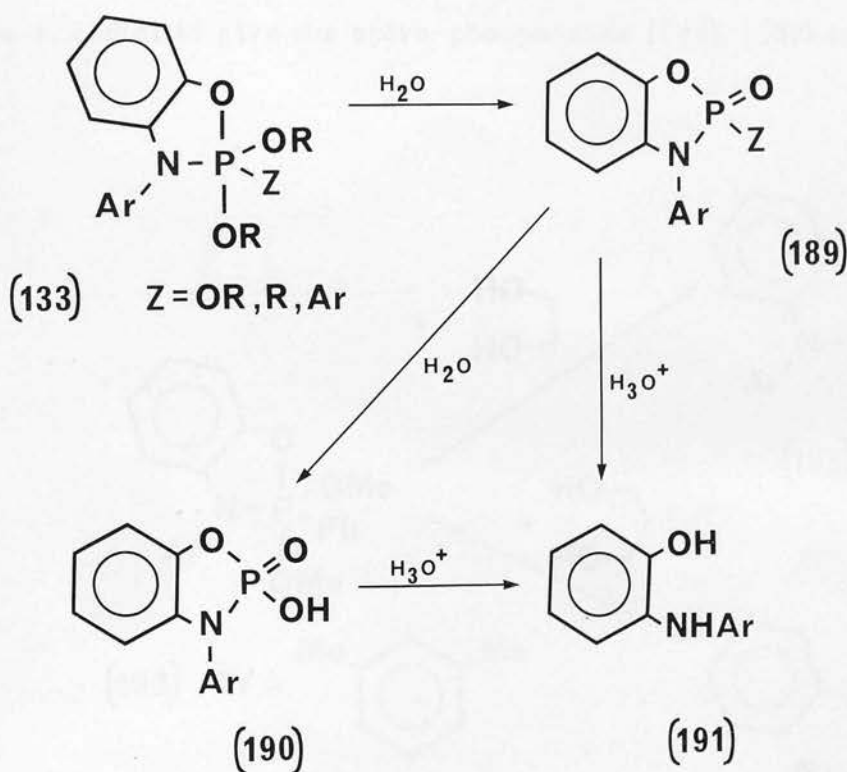
crystallography, and lends strong support to the postulate that unstable 1,3,2-benzothiazaphosph(v)oles (185) are formed by the reaction of trivalent phosphorus reagents with 2,6-disubstituted phenyl 2-nitrophenyl sulphides.

The deoxygenation of 1-(2-nitrobenzyl)-2,4,6-trimethylbenzene (137; scheme 68) by triethyl phosphite, as described in section A. 2(f), gives 7% of the diethylbenzylphosphonate (139). It has been suggested^{58b} that this may arise either via the zwitterion (188) or via the 1,2-benzazaphosph(v)ole (187), but as yet no firm conclusions have been published.



B. 2(b) Reactions of 3-Aryl-2,3-dihydro-1,3,2-benzoxazaphosph(v)oles

(i) Hydrolysis. The 1,3,2-benzoxazaphosph(v)oles (133) are very susceptible to hydrolysis, and even when great care is taken to exclude water during their preparation the compounds are sometimes contaminated with their hydrolysis products.^{58,82} Hydrolysis of 2,2,2-trialkoxy-derivatives proceeds in three steps,^{58a} as outlined in scheme 110. The first step, to give a 2-substituted 3-aryl-2,3-dihydro-2-oxo-



Scheme 110

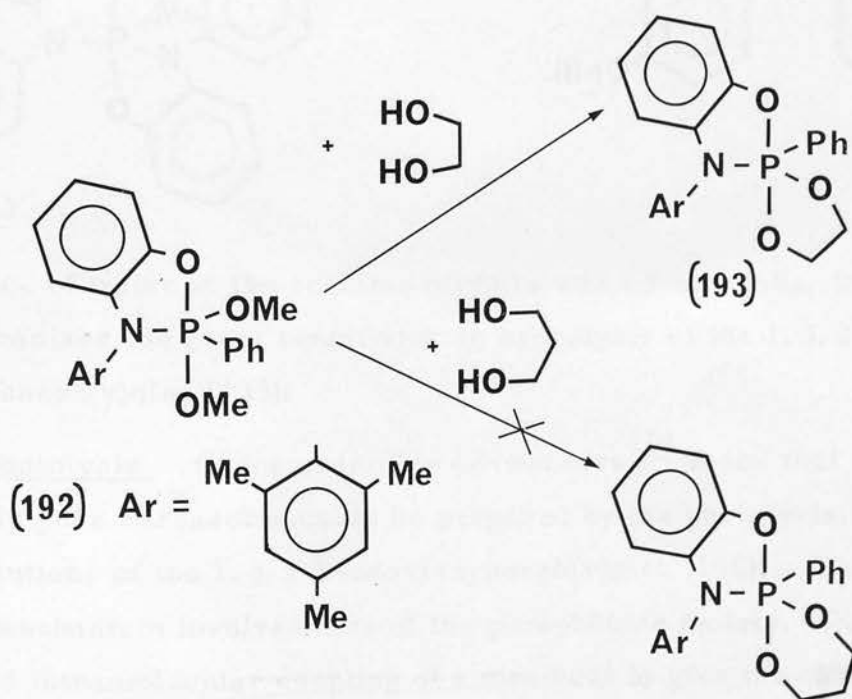
1,3,2-benzoxazaphosph(v)ole (189), occurs during recrystallisation, when this is not performed in a perfectly dry atmosphere. If the compound (189) is allowed to stand under normal atmospheric conditions, the remaining 2-substituent is lost by hydrolysis to give compound (190). The final stage of hydrolysis, which is readily accomplished by boiling a solution of the 1,3,2-benzoxazaphosph(v)ole (133), or compound (190), in ethanol/dilute hydrochloric acid for 16 h, gives a 2-anilinophenol (191).

An example of compound (190), 2,3-dihydro-3(2',6'-dimethyl-

phenyl)-2-hydroxy-2-oxo-1,3,2-benzoxazaphosph(v)ole, has been examined by X-ray crystallography, which confirmed the assigned structure and showed that the geometry was that of a distorted tetrahedron.¹⁰²

1,3,2-Benzoxazaphosph(v)oles (181) derived from phosphonites, such as $(\text{MeO})_2\text{PPh}$, also undergo rapid hydrolysis to give 2-alkyl (or aryl)-3-aryl-2,3-dihydro-2-oxo-1,3,2-benzoxazaphosph(v)oles (189; $\text{Z}=\text{R}$ or Ar) and 2-anilinophenols (191).^{58a}

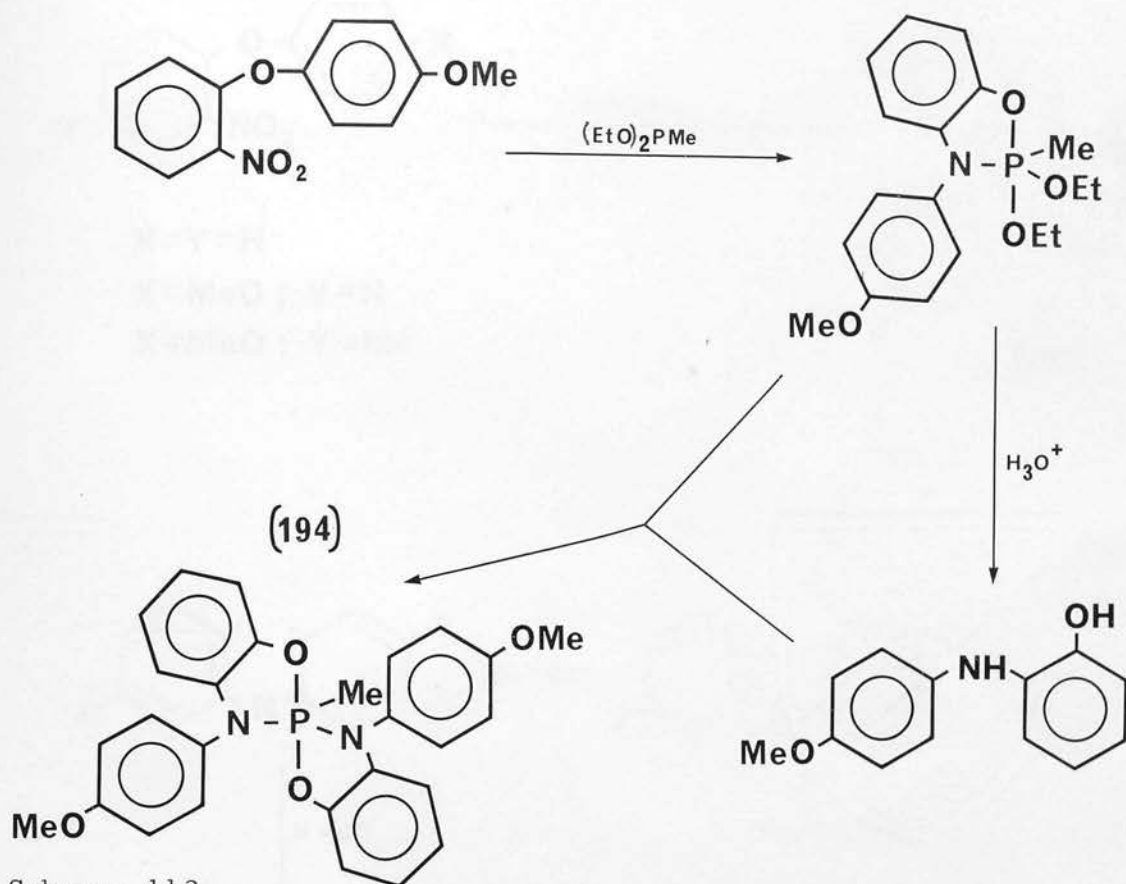
(ii) Ligand exchange. A ligand-exchange, or transesterification, reaction has been observed^{58a} in the case of 2,3-dihydro-2,2-dimethoxy-3-mesityl-2-phenyl-1,3,2-benzoxazaphosph(v)ole (192), which reacts with ethane-1,2-diol to give the spiro-phosphorane (193), (Scheme 111).



Scheme 111

However, (192) does not react with propane-1,3-diol, thus illustrating the increased stability of a phosphorane incorporating a five-membered ring, compared to one incorporating a six-membered ring.^{58a}

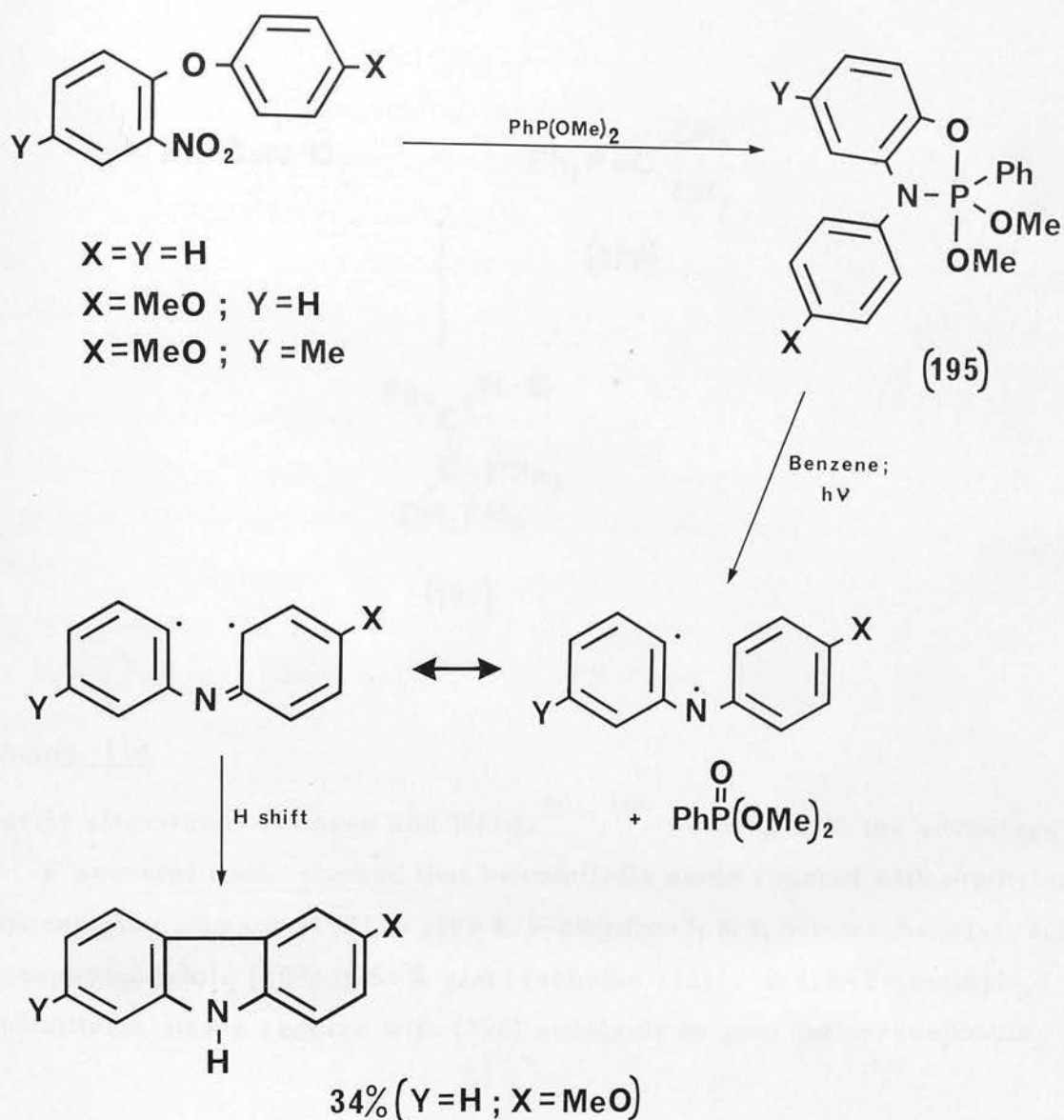
Hydrolysis and ligand-exchange reactions have both been invoked to explain the formation of the spiro-phosphorane (194) (19.5%) during the deoxygenation of 4-methoxyphenyl 2-nitrophenyl ether by diethyl methyl phosphonite, $(\text{EtO})_2\text{PMe}$,^{58a} as illustrated by scheme 112.



Scheme 112

The presence of water in the reaction mixture was adventitious, but the result emphasises the great sensitivity to hydrolysis of the 1, 3, 2-benzoxazaphosph(v)oles (133).

(iii) Photolysis. Cadogan and his co-workers¹⁰⁴ found that isomerically pure carbazoles could be prepared by the photolysis, in benzene solution, of the 1, 3, 2-benzoxazaphosph(v)oles (195). The suggested mechanism involves loss of the phosphonate moiety, $\text{PhP}(\text{O})(\text{OMe})_2$, and intramolecular coupling of a diradical to give the carbazole, as described in scheme 113.



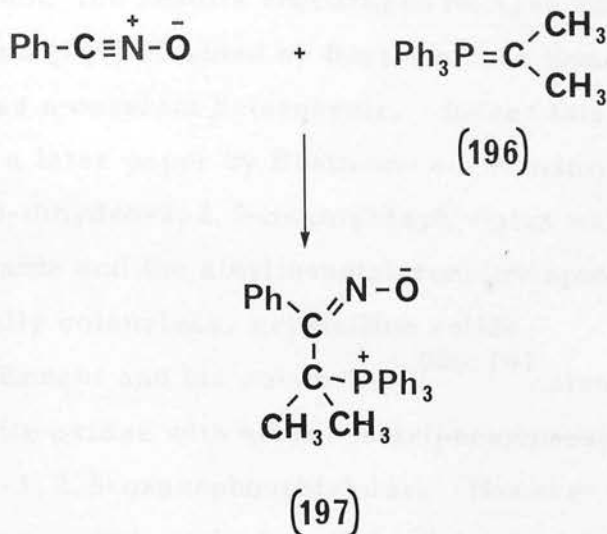
Scheme 113

B. 3 1, 2, 5-Oxazaphosph(v)oles

B. 3(a) Preparation and Structure

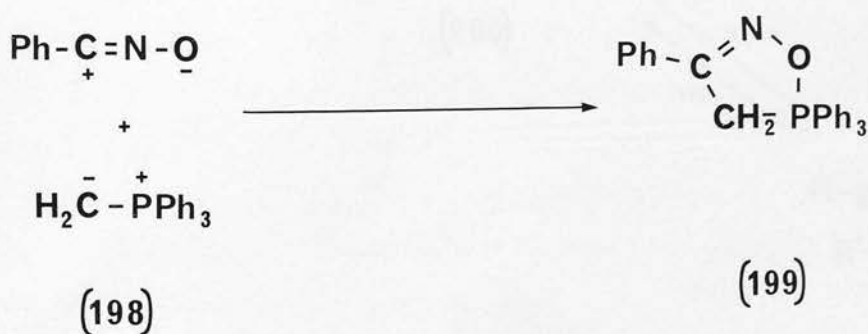
(i) Reaction of phosphorus ylides with nitrile oxides, and the cyclisation of 2-oximinophosphonium salts. Bestmann and Kunstmann¹⁰⁵

first reported the reaction of benzonitrile oxide with isopropylidenetriphenylphosphorane (196) and suggested that the adduct had a zwitterionic form (197) (Scheme 114).



Scheme 114

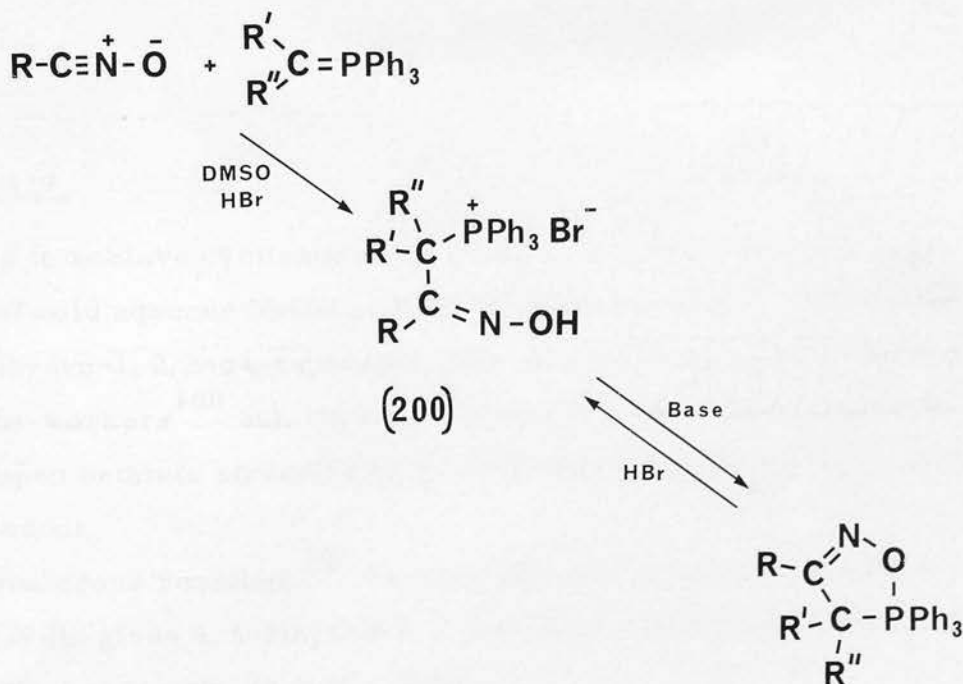
Shortly afterwards Huisgen and Wulff,^{98a, 106} working with the advantage of ^{31}P spectral data, showed that benzonitrile oxide reacted with methylene-triphenylphosphorane (198) to give 4, 5-dihydro-3, 5, 5, 5-tetraphenyl-1, 2, 5-oxazaphosph(v)ole (199) in 66% yield (scheme 115). 2, 4, 6-Trimethylbenzonitrile oxide reacted with (198) similarly to give the corresponding



Scheme 115

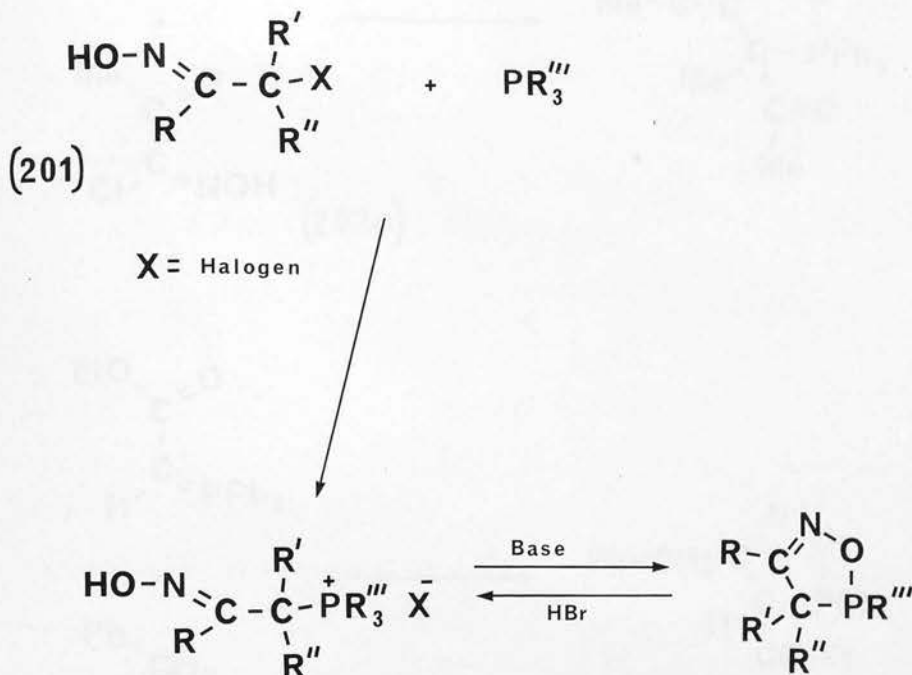
cyclic adduct in 71% yield. Although the reaction of benzonitrile oxide with benzylidene triphenylphosphorane, PhCH=PPh_3 , failed to give an isolable adduct, the results encouraged Huisgen and Wulff to suggest that compound (197) obtained by Bestmann and Kunstmann might be better formulated as a covalent heterocycle. Indeed this point was apparently conceded in a later paper by Bestmann and Kunstmann,^{98c} in which a larger range of 4, 5-dihydro-1, 2, 5-oxazaphosph(v)oles was prepared by varying both the nitrile oxide and the alkylidenetriphenylphosphorane. These compounds were generally colourless, crystalline solids.

Umani-Ronchi and his co-workers^{98b, 107} also examined the reaction of benzonitrile oxides with alkylidenetriphenylphosphoranes and obtained 4, 5-dihydro-1, 2, 5-oxazaphosph(v)oles. However they found that if the reaction was carried out in dimethyl sulphoxide, in the presence of HBr, a 2-oximinophosphonium salt (200) was obtained. Treatment of the salt with base gave the 4, 5-dihydro-1, 2, 5-oxazaphosph(v)ole, a reaction which could be reversed by treatment with HBr (scheme 116).



Scheme 116

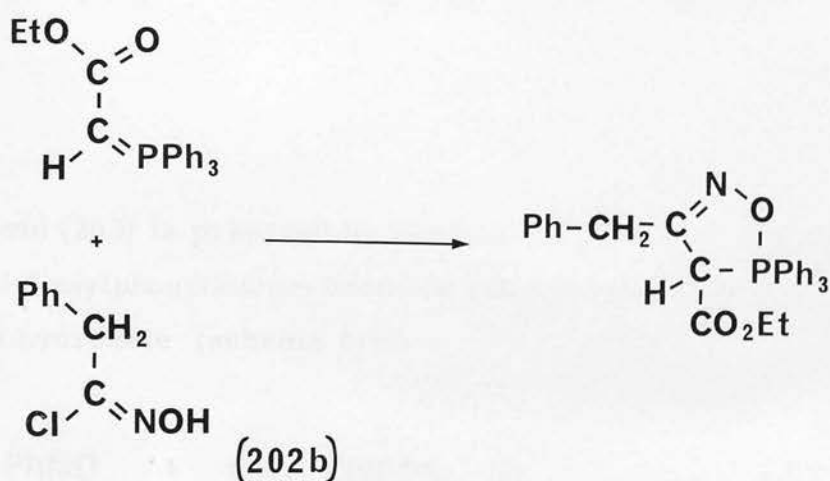
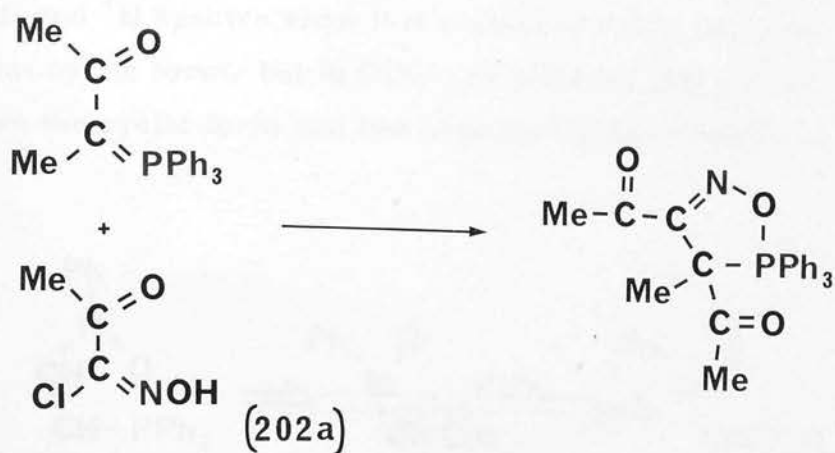
A second, more versatile route^{98a} to the 2-oximinophosphonium salts was the reaction of tertiary phosphines with α -halo-oximes (201) (scheme 117). Cyclisation of this greater range of salts led to the preparation of several new 4, 5-dihydro-1, 2, 5-oxazaphosph(v)oles. The



Scheme 117

base used to achieve cyclisation was preferably a basic ion-exchange resin, but cold aqueous NaOH or KOH was also effective. This route to 4, 5-dihydro-1, 2, 5-oxazaphosph(v)oles was also reported by Masaki and his co-workers¹⁰⁸ but, lacking ^{31}P spectral data, they suggested that the open betainic structure (e.g. 197) might contribute to the structure of the product.

An analogous reaction,¹⁰⁹ between phosphorus ylides and chloro-oximes (202), gives 4, 5-dihydro-1, 2, 5-oxazaphosph(v)oles in unstated yield in two cases only (scheme 118).

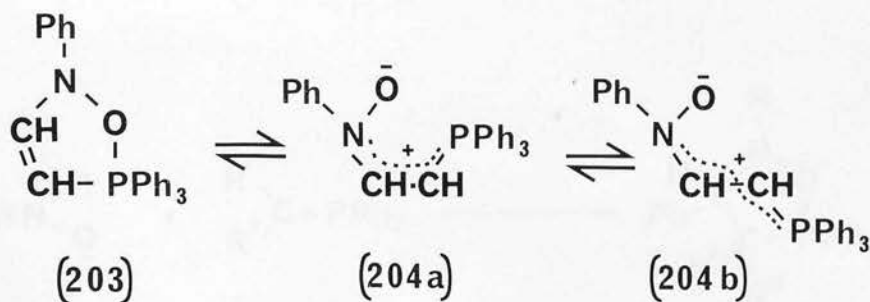


Scheme 118

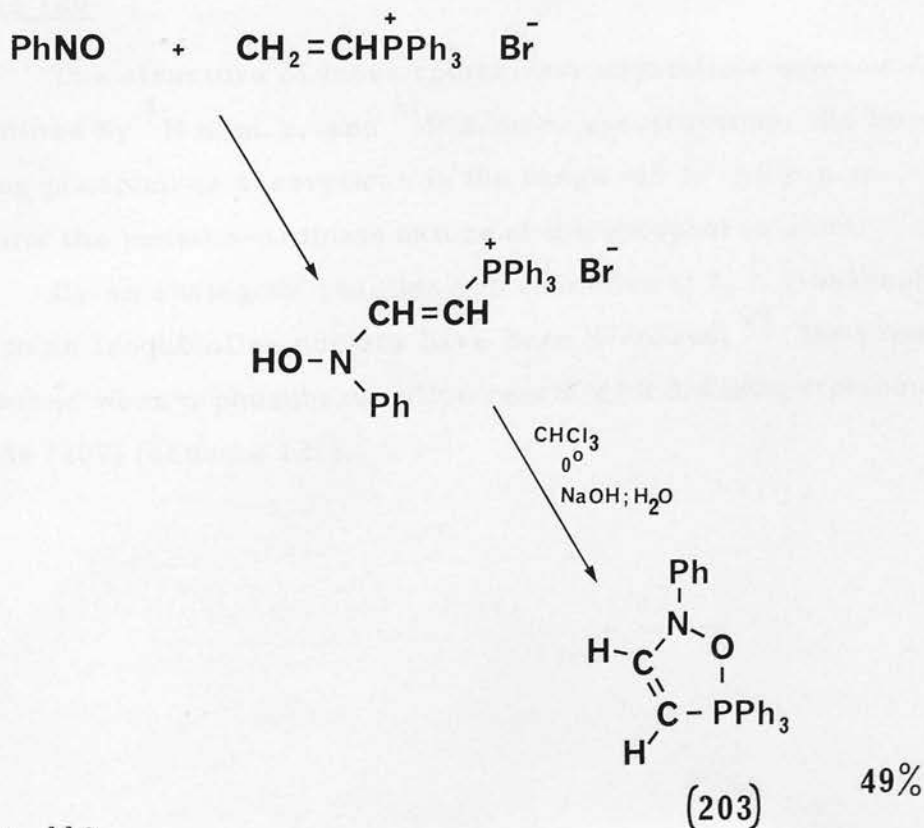
Whenever ^{31}P spectral data have been available, negative shift values for the phosphorus absorptions have shown that the phosphorus atom is pentaco-ordinate, supporting the covalent heterocyclic structure (e. g. 199). A detailed ^1H n.m.r. study^{98b} and comparison of the spectra of 2-oximinophosphonium salts and the corresponding 4, 5-dihydro-1, 2, 5-oxazaphosph(v)oles also gave results which supported a cyclic structure for the latter compounds.

It had been shown,¹¹⁰ however, that the structure of a related compound, 2, 5-dihydro-2, 5, 5, 5-tetraphenyl-1, 2, 5-oxazaphosph(v)ole (203)

is solvent dependent. In non-polar solvents, such as CCl_4 or benzene- d_6 , the ^{31}P and ^1H spectra show that compound (203) exists solely in the covalent cyclic form, but in CDCl_3 or alcohols there is an equilibrium between the cyclic form and two betainic forms, (204a) and (204b). The

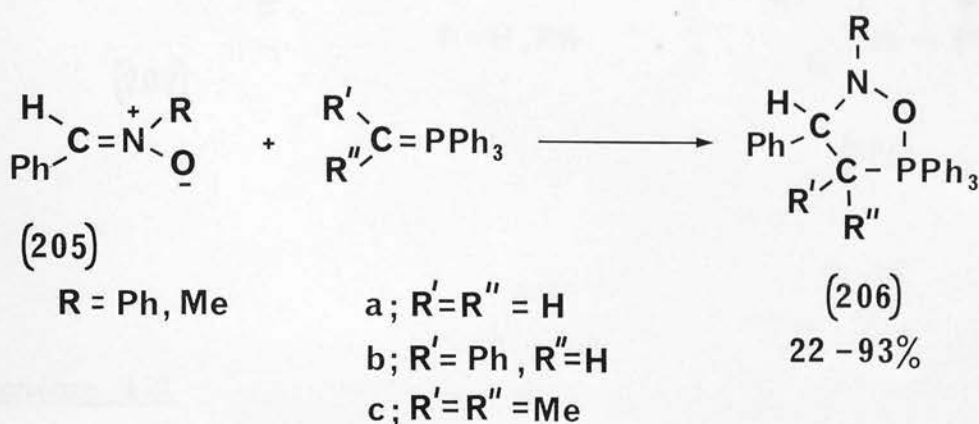


compound (203) is prepared by treating the product of the reaction between vinyltriphenylphosphonium bromide and nitrosobenzene with aqueous sodium hydroxide (scheme 119).



Scheme 119

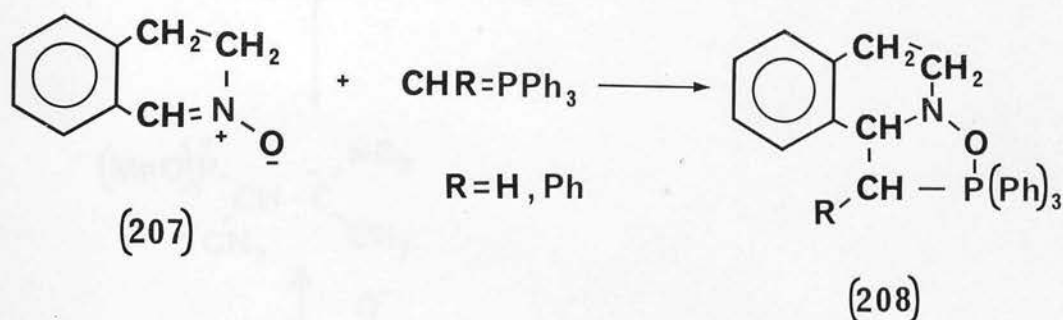
(ii) Reaction of phosphorus ylides with nitrones. 1, 3-Cyclo-additions of C-phenylnitrones (205) to alkylidenetriphenylphosphoranes has been found⁹⁹ to occur readily in ether solvent, at 20°, to give fully saturated heterocyclic compounds, 3, 5, 5, 5-tetraphenyl-1, 2, 5-oxazaphosph(v)olidines (206) (scheme 120).



Scheme 120

The structure of these colourless, crystalline compounds was determined by ¹H n.m.r. and ³¹P n.m.r. spectroscopy, the latter showing phosphorus absorptions in the range -45 to -60 p.p.m., which confirms the pentaco-ordinate nature of the phosphorus atom.

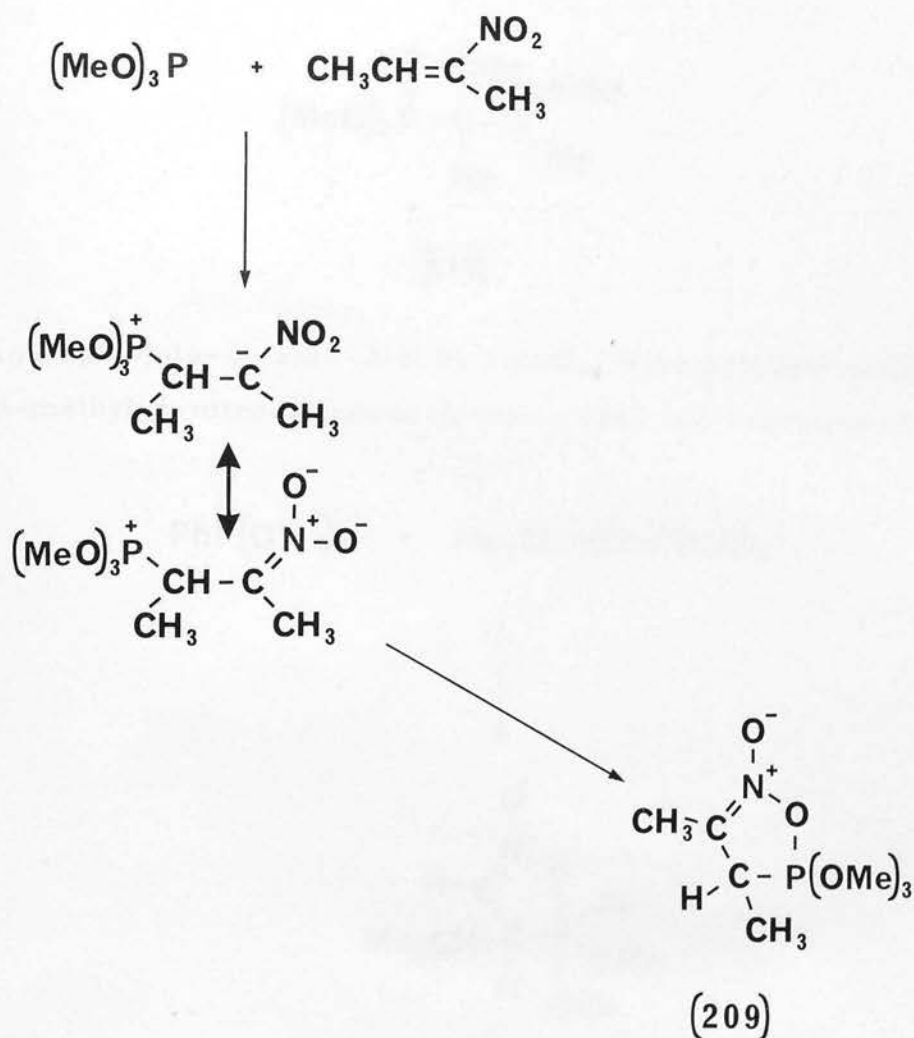
By an analogous reaction two examples of 1, 2, 5-oxazaphosph(v)olidines fused to an isoquinoline nucleus have been prepared.⁹⁹ The product (208) is obtained when a phosphorus ylide reacts with 3,4-dihydroisoquinoline N-oxide (207) (scheme 121).



Scheme 121

(iii) Reaction of tervalent phosphorus reagents with 1-nitro-olefins. In certain cases the reaction of a tervalent phosphorus reagent with a 1-nitro-olefin can result in the formation of an isolable phosph(v)ole. For example, Gareev and his co-workers¹¹¹ showed that reaction of trimethyl phosphite with 2-nitro-2-butene, under mild conditions in an aprotic solvent, gave 88% of the solid 4, 5-dihydro-3, 4-dimethyl-5, 5, 5-trimethoxy-1, 2, 5-oxazaphosph(v)ole-2-oxide (209). Gareev suggested that reaction occurred via Michael-type addition of the $(\text{MeO})_3\text{P}$ to the activated double bond, leading to a 1, 5-dipole which then cyclised to give the observed product (scheme 122).

The assigned structure of this adduct was supported by the spectral data available. ³¹P n. m. r. spectra recorded in benzene or acetone as solvent showed a single absorption at -34 p. p. m. or -38 p. p. m. respectively. Absorptions in this range are indicative of a pentaco-ordinate phosphorus atom, and the small change in the shift on changing from a solvent of low polarity to one of high polarity shows that there is no tendency for the phosph(v)ole ring to open to give a betainic structure. ^{87a}

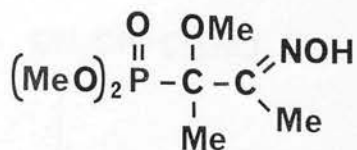


Scheme 122

The proton n. m. r. spectrum showed a complete magnetic equivalence of the three P-methoxy-groups, which resonate as a doublet at $\delta = 3.45$ p. p. m. (relative to internal T. M. S.) with a coupling constant of $^3J = 13.0\text{Hz}$. The infra-red spectrum was also of note for the absorptions at 1265 and 1633 cm^{-1} ascribed to N^+-O^- and $\text{C}=\text{N}$ bond vibrations respectively, and for the absence of an absorption band which could be ascribed to $\text{P}=\text{O}$ bond vibrations.

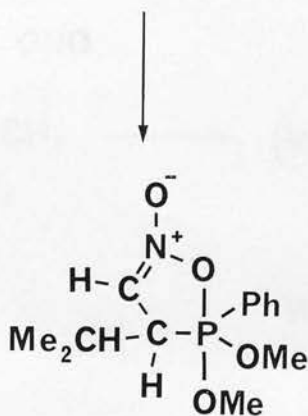
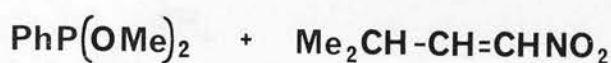
It was found¹¹² that a high concentration of reactants was required to form the phosph(v)ole (209), otherwise an oxime (210) was obtained.

Gareev and his co-workers¹¹³ also succeeded in obtaining a 1, 2, 5-



(210)

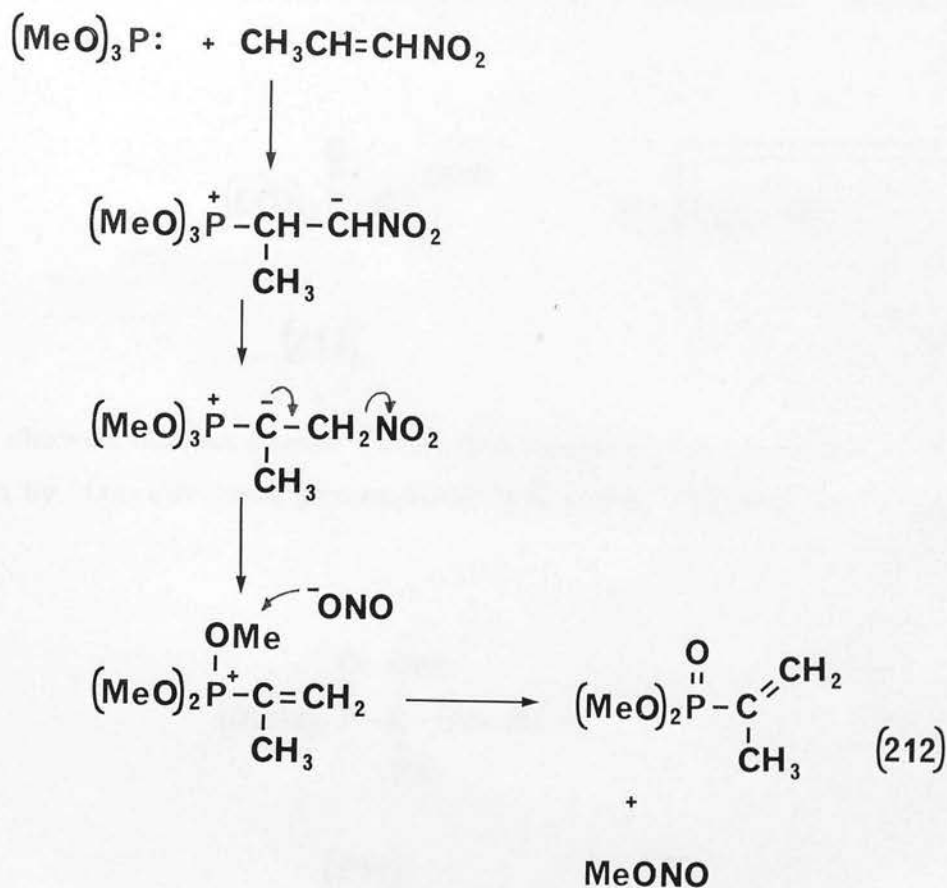
oxazaphosph(v)ole-2-oxide (211) by reacting dimethylphenylphosphonite with 3-methyl-1-nitro-1-butene (scheme 123), but reactions of tervalent



(211)

Scheme 123

phosphorus reagents with 1-nitropropene gave various open-chain phosphonate esters, depending on reactants and conditions. For example, from the reaction between trimethyl phosphite and 1-nitropropene, dimethyl *iso*-propenylphosphonate (212) was obtained in 80% yield.¹¹⁴ Gareev suggested that the intermediate 1, 3-dipolar ion was stabilised by proton transfer and loss of methyl nitrite, rather than by ring closure (scheme 124). The reaction of 2-nitro-2-butene with trimethyl phosphite, (scheme 122) does not follow this pathway, possibly because of a hyper-conjugation effect of the α -methyl group which increases the stability of the dipolar intermediate, making the transfer of a proton less favourable.

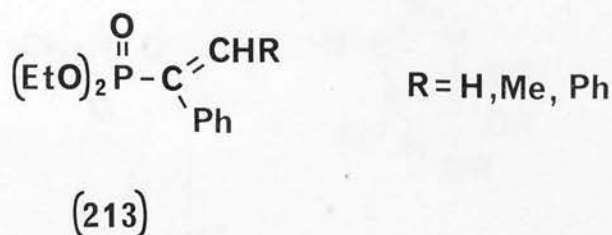


Scheme 124

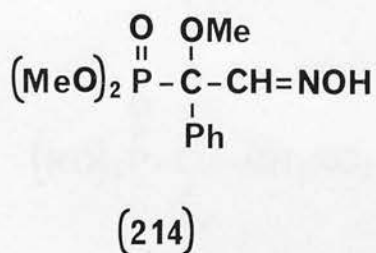
The Russian workers have made detailed studies of the reactions between simple aliphatic nitro-olefins and tervalent phosphorus reagents.^{111-114, 115} Their results strongly suggest that nucleophilic attack of the phosphorus reagent at a double-bond activated by a nitro-group is an energetically favourable reaction, but that subsequent ring closure to give an isolable 1, 2, 5-oxazaphosph(v)ole-2-oxide only occurs under special circumstances, in a few cases.

The impressions formed by a study of the work described above are strengthened by the reported results of reactions between tervalent phosphorus reagents and aromatic nitro-olefins. Krueger and his co-workers¹¹⁶ found that one of the products from attempted deoxygenations of α -substituted- β -nitrostyrenes by triethyl phosphite was the diethyl-

phosphonate ester (213). A later study¹¹⁷ of the reaction between β -nitrostyrene and trimethyl phosphite at room temperature in t-butanol

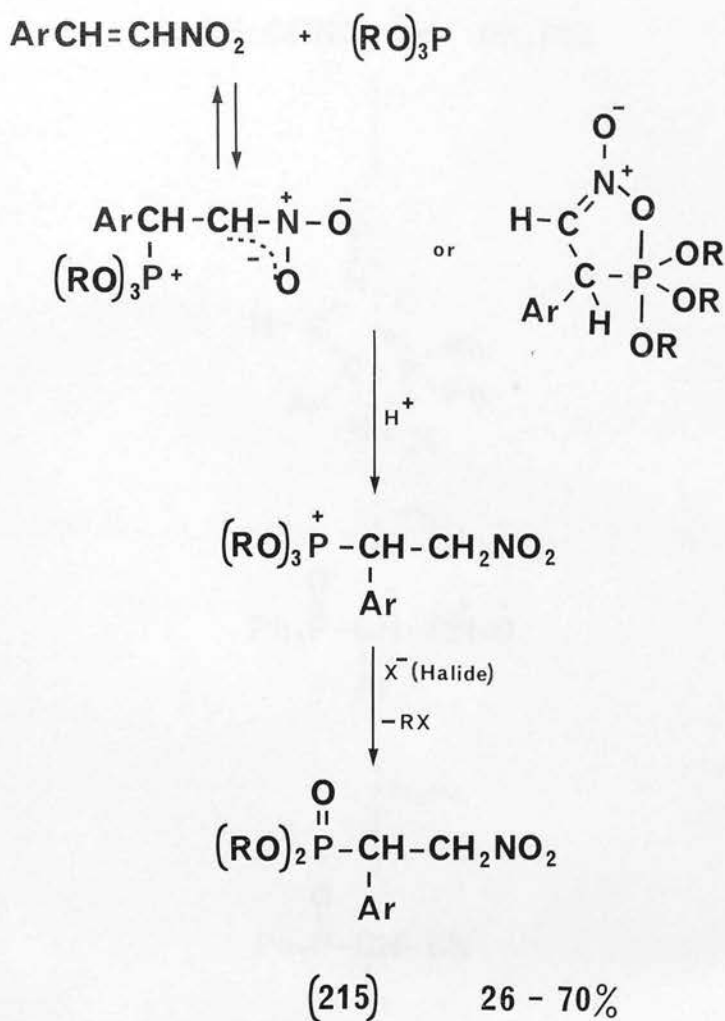


solvent showed that an oxime (214), analogous to the compound (210) obtained by Gareev, was produced in 34% yield. In addition methyl



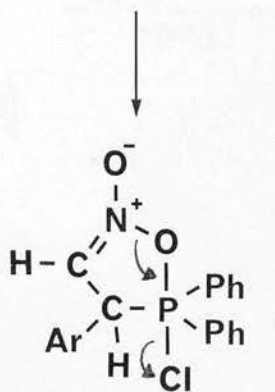
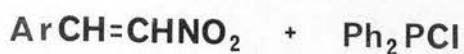
nitrite and an unidentified red oil were obtained.

A more comprehensive study¹¹⁸ of the reaction between β -nitrostyrenes and phosphites has shown that, although 1, 2, 5-oxazaphosph(v)ole-2-oxides may be intermediates, the final products are phosphonate esters (215) in which the nitro-group is retained (scheme 125).

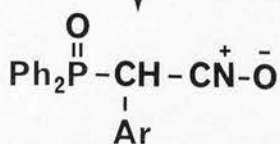


Scheme 125

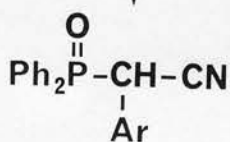
Similarly, a P-chloro-1, 2, 5-oxazaphosph(v)ole-2-oxide has been postulated as an intermediate in the reaction of β -nitrostyrenes with diphenylchlorophosphine (scheme 126).¹¹⁹



-HCl

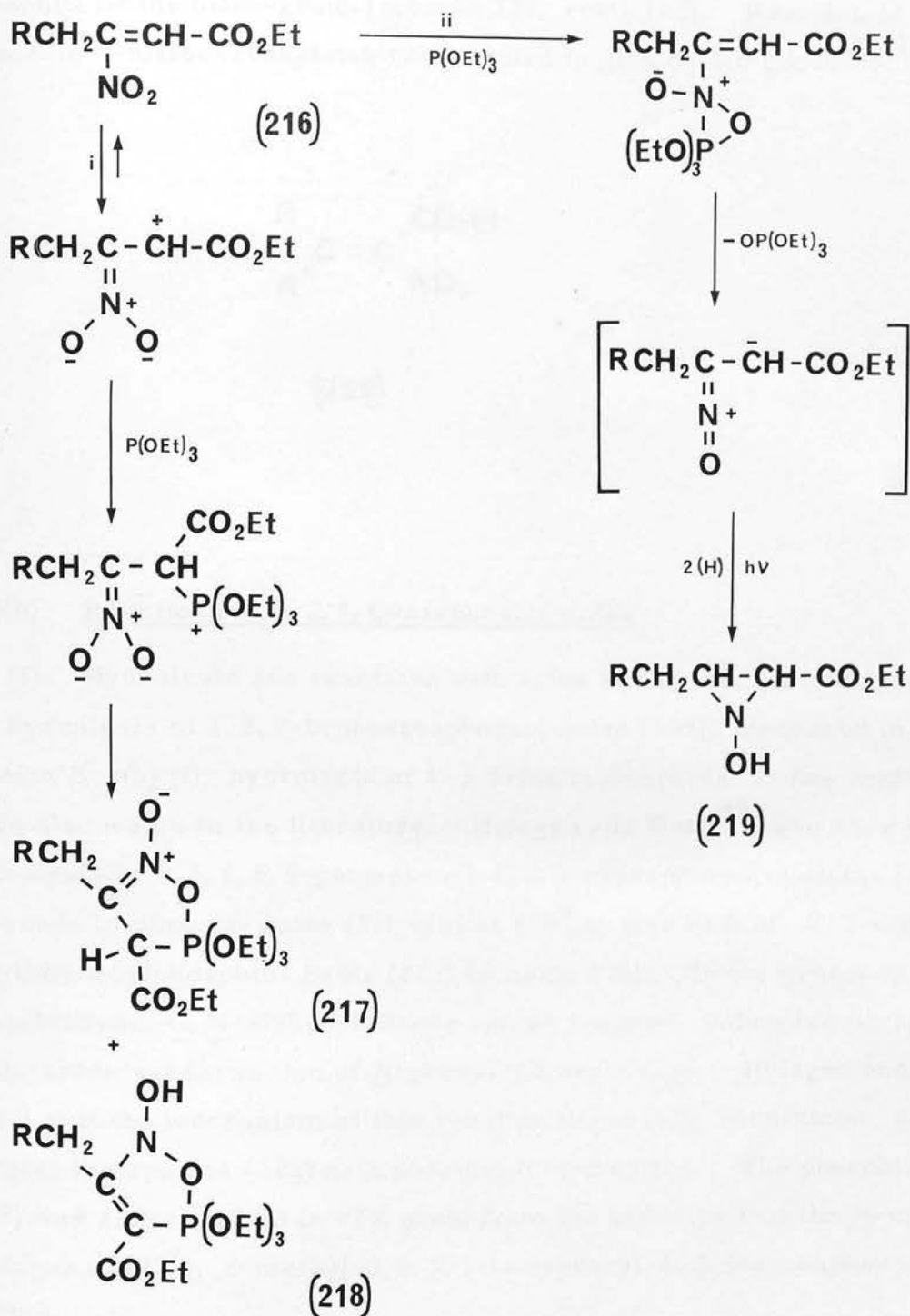


Ph_2PCI



Scheme 126

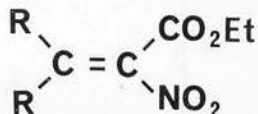
Shin and his co-workers¹²⁰ have prepared a series of 1, 2, 5-oxazaphosph(v)oles by the reaction of triethyl phosphite with ethyl α, β -unsaturated β -nitrocarboxylates (216) [scheme 127, route (i)]. A notable feature of these compounds is that n.m.r. studies have shown that they are isolated as a mixture of isomers, 4, 5-dihydro-1, 2, 5-oxazaphosph(v)ole-2-oxide



Scheme 127

(217) and 2,5-dihydro-2-hydroxy-1,2,5-oxazaphosph(v)ole (218). It is suggested that the formation of an aziridine (219) in the same reaction may

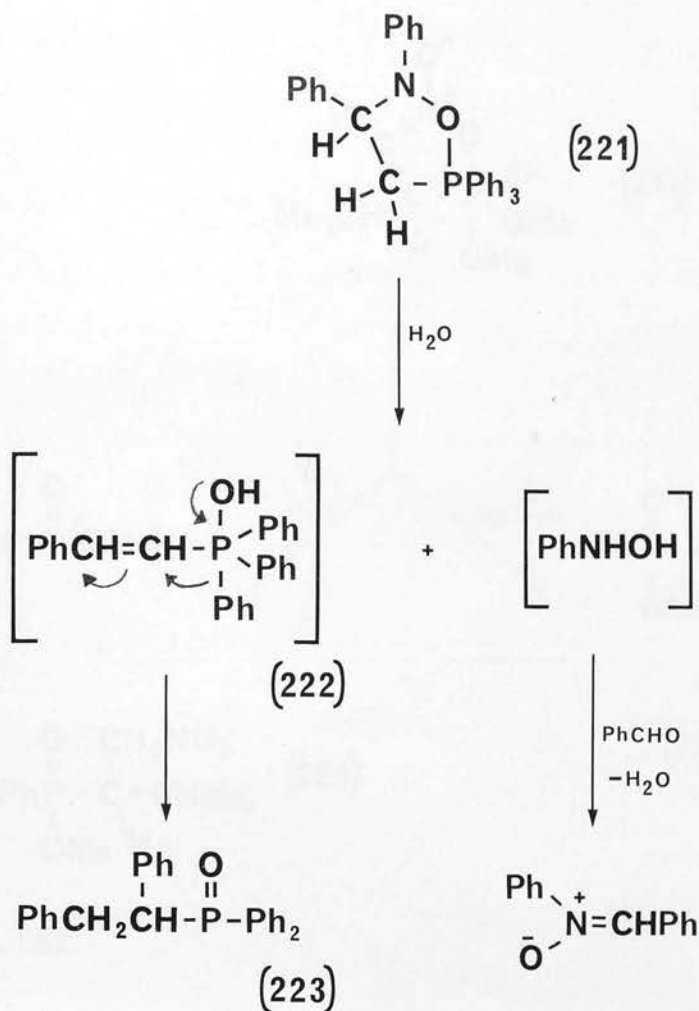
occur by an alternative pathway, via the more familiar initial attack of phosphite at the nitro-group [scheme 127, route (ii)]. Reaction of the isomeric α -nitrocarboxylates (220) failed to give cyclic products.¹²¹



(220)

B. 3(b) Reactions of 1, 2, 5-Oxazaphosph(v)oles

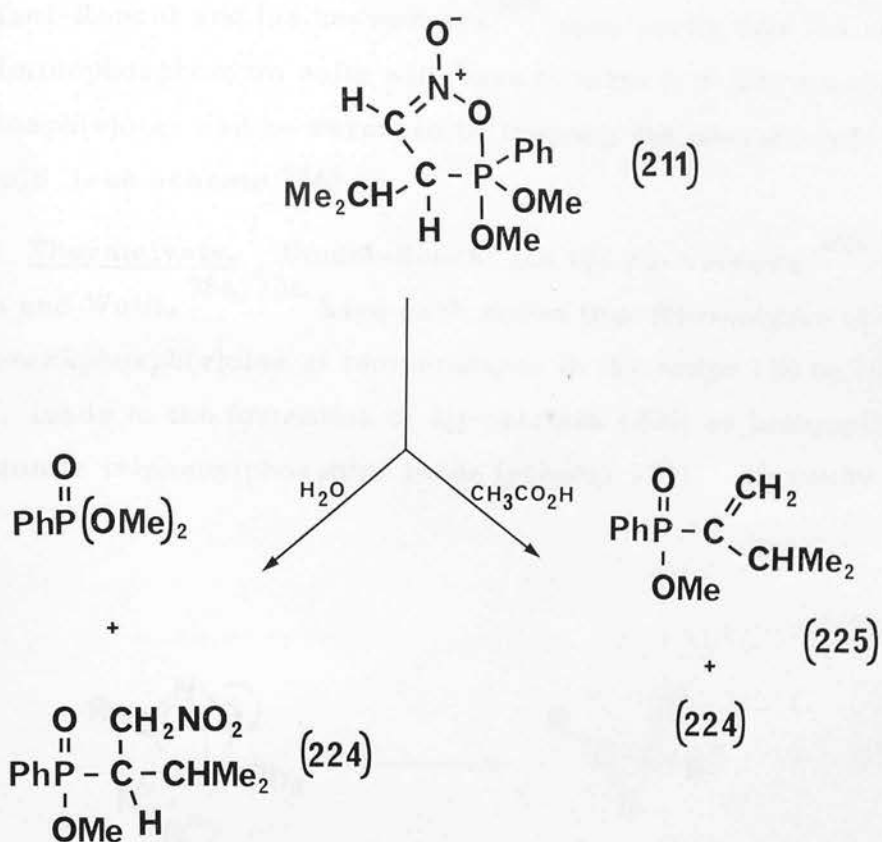
(i) Hydrolysis and reactions with acids and bases. Compared to the hydrolysis of 1, 3, 2-benzoxazaphosph(v)oles (133), discussed in section B. 2(b) (i), hydrolysis of 1, 2, 5-oxazaphosph(v)oles has merited little discussion in the literature. Huisgen and Wulff⁹⁹ have shown that hydrolysis of 2, 3, 5, 5, 5-pentaphenyl-1, 2, 5-oxazaphosph(v)olidine (221) proceeds in dioxane-water (5:1 v/v) at 100° to give 81% of (1, 2-diphenyl-ethyl)diphenylphosphine oxide (223) (scheme 128). In the presence of benzaldehyde, C, N-diphenylnitrone can be isolated, indicative perhaps of the transient formation of N-phenylhydroxylamine. Huisgen and Wulff admit that the mechanism of this reaction is not fully understood, but suggest the species (222) as a possible intermediate. The phosphine oxide (223) was also obtained in 43% yield from the hydrolysis of the N-methyl analogue of (221), 2-methyl-3, 5, 5, 5-tetraphenyl-1, 2, 5-oxazaphosph(v)-olidine.



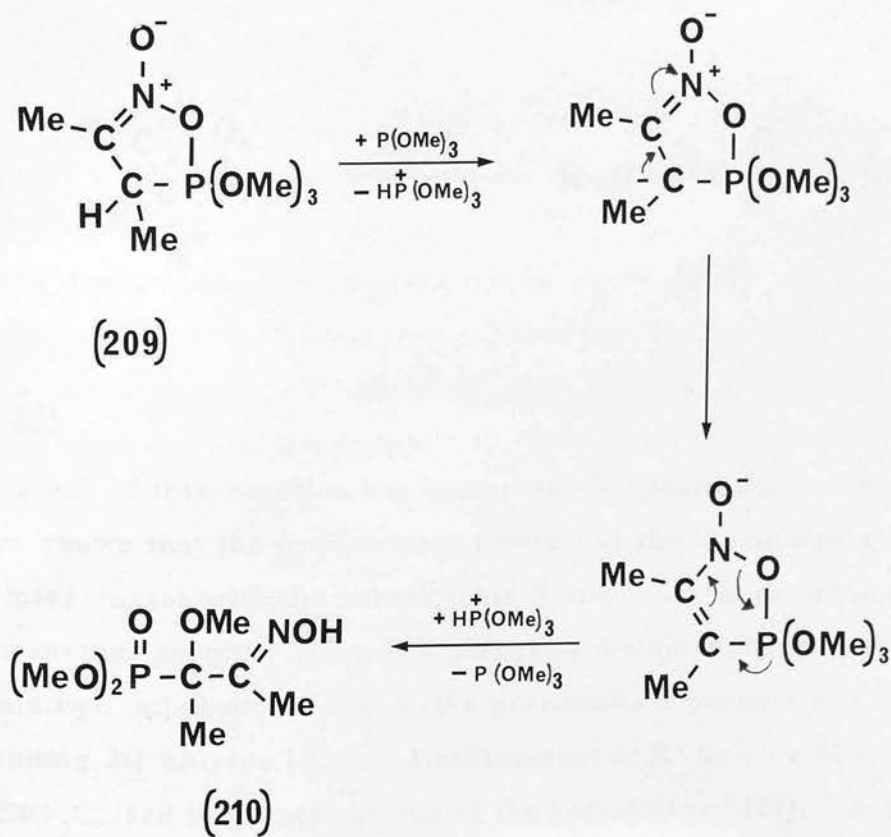
Scheme 128

The hydrolysis of a 1, 2, 5-oxazaphosph(v)ole-2-oxide (211) has been described briefly by Gareev and his co-workers.¹¹³ In the presence of water, hydrolysis proceeds readily to give a phosphinate ester (224) and dimethylphenylphosphonate. The ester (224) is also produced, in addition to a second phosphinate ester (225) in which the nitro-group has been lost, when the phosph(v)ole (211) reacts with acetic acid (scheme 129).

Gareev and his co-workers^{115a} also suggest that the 1, 2, 5-oxazaphosph(v)ole-2-oxide (209) reacts with trimethyl phosphite acting as a base, to give the oxime (210) (scheme 130).



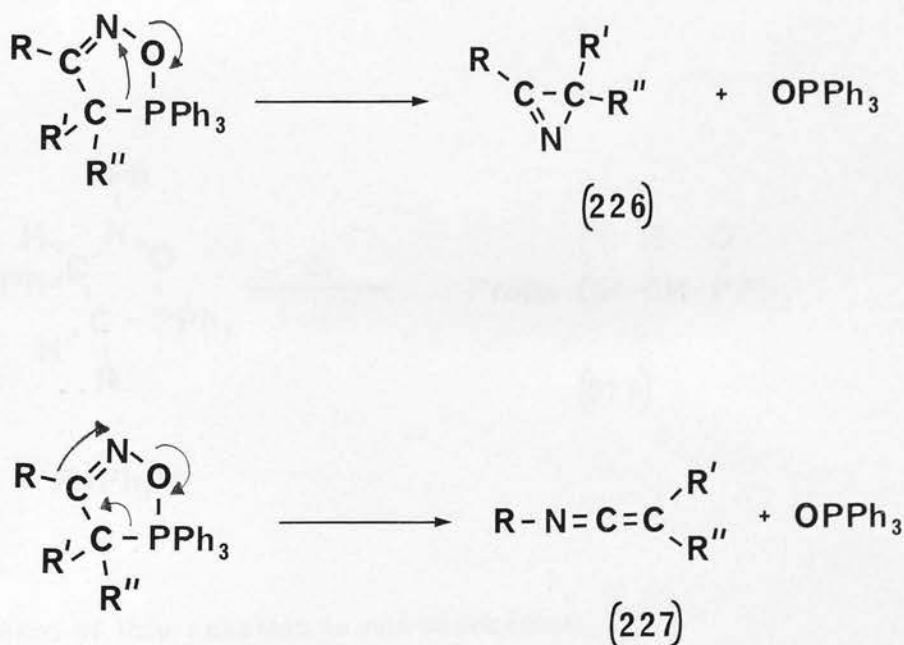
Scheme 129



Scheme 130

Umani-Ronchi and his co-workers^{98b} have shown that the reaction of 2-oximinophosphonium salts with base to form 4, 5-dihydro-1, 2, 5-oxazaphosph(v)oles can be reversed by treating the phosph(v)ole with HBr in the cold (see scheme 116).

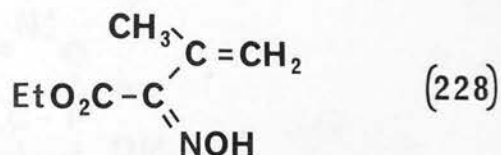
(ii) Thermolysis. Umani-Ronchi and his co-workers,^{98b} and Huisgen and Wulff,^{98a, 106} have each shown that thermolysis of 4, 5-dihydro-1, 2, 5-oxazaphosph(v)oles at temperatures in the range 120 to 150°, under vacuum, leads to the formation of 2H-azirines (226) or ketenimines (227), in addition to triphenylphosphine oxide (scheme 131). However the most



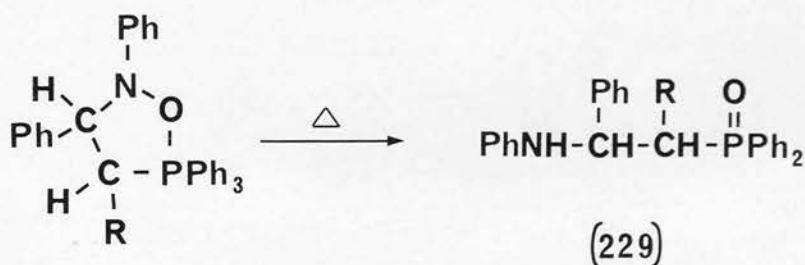
Scheme 131

thorough study of this reaction has been made by Bestmann and Kunstmann.^{98c} They have shown that the predominant product of the thermolysis of these phosph(v)oles varies with the substituents R and R'. In each case studied R'' was a methyl group. When R = phenyl or 4-chlorophenyl and R' = phenyl, methyl, ethyl or hydrogen, the predominant product was the corresponding 2H-azirine (226). Replacement of R' by an ethoxycarbonyl group, EtO₂C, led to greater yields of the ketenimine (227). A further

product, a 3-oximinoalkene (228), was obtained when $R = \text{EtO}_2\text{C}$ and $R' = R'' = \text{methyl}$.



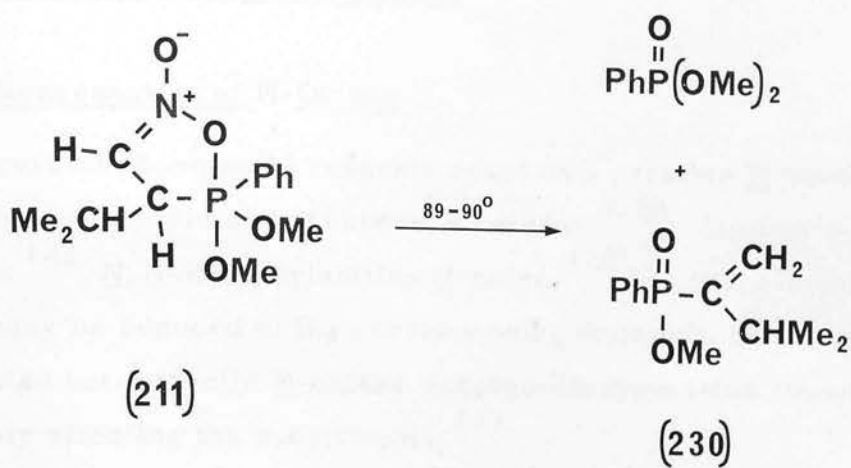
Huisgen and Wulff⁹⁹ have shown that 1, 2, 5-oxazaphosph(v)-olidines decompose thermally in boiling xylene with loss of C_6H_4 to give a phosphine oxide (229) in 24 to 38% yield (scheme 132).



Scheme 132

The mechanism of this reaction is not understood.

Gareev and his co-workers¹¹³ have shown that thermolysis of 4, 5-dihydro-5, 5-dimethoxy-4-isopropyl-5-phenyl-1, 2, 5-oxazaphosph(v)ole-2-oxide (211) gives both dimethylphenylphosphonate and a vinyl phosphinate ester (230) (scheme 133).



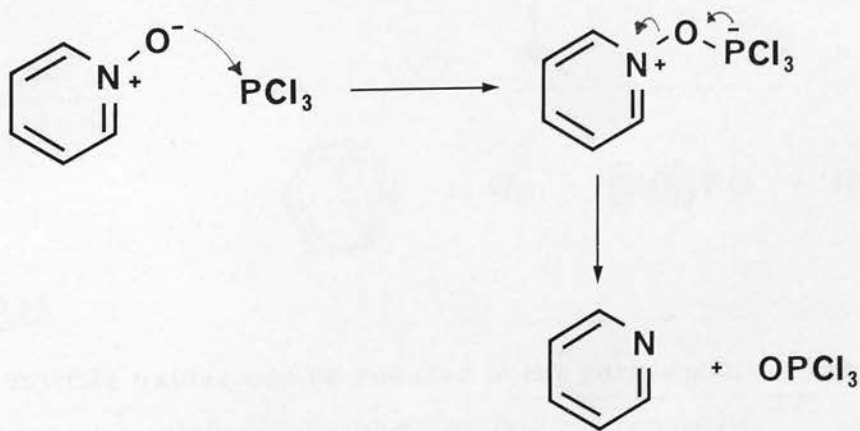
Scheme 133

C The Deoxygenation of N-Oxides and Nitroxyl Radicals by Tervalent Phosphorus Reagents

C.1 Deoxygenation of N-Oxides

Tervalent phosphorus reagents react with pyridine N-oxide to give pyridine and the oxidised phosphorus reagent.^{9, 10} Similarly quinoline N-oxide,¹²² N, N-dimethylaniline N-oxide,¹²² and trimethylamine N-oxide⁷ may be reduced to the corresponding amines. In general, substituted heterocyclic N-oxides undergo deoxygenation smoothly without adversely affecting the substituents.¹²³

In contrast to the reactions with nitro- and nitroso-groups, the reactivity of the phosphorus reagents decreases in the order $\text{PCl}_3 > \text{PhPCl}_2 > \text{Ph}_2\text{PCl} \gg (\text{PhO})_3\text{P} > (\text{EtO})_3\text{P} \gg \text{Ph}_3\text{P} > \text{Bu}_3\text{P}$.¹²⁴ In view of the electrophilic characteristics of PCl_3 and the observed lowering of reactivity which coincides with the replacement of chlorine atoms by electron-releasing groups, these results indicate that deoxygenation of the pyridine N-oxide occurs by electrophilic attack of the phosphorus reagent at the oxygen atom (scheme 134). This mechanism is supported

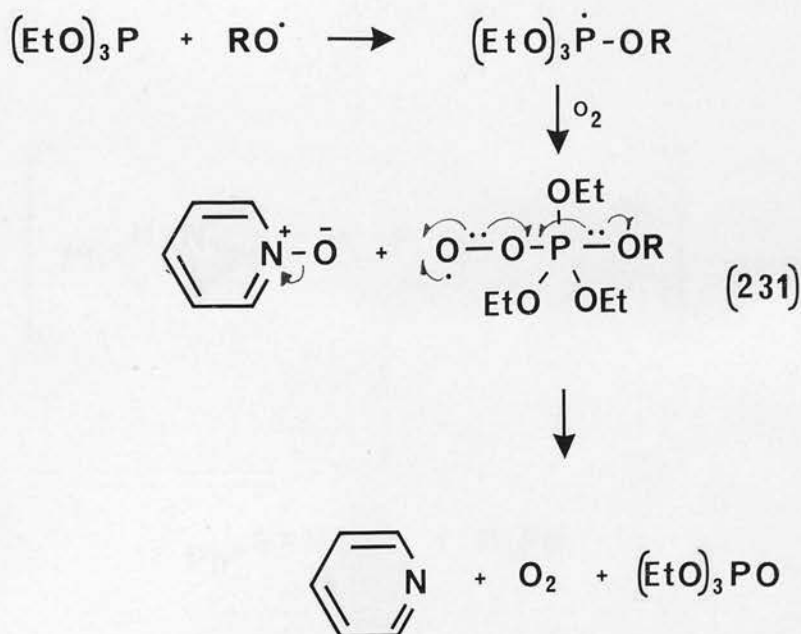


Scheme 134

by the observation¹²⁵ that 4-nitropyridine N-oxide, in which the electron density at the oxygen atom is reduced relative to pyridine N-oxide, is

reduced less readily by PCl_3 than is pyridine N-oxide. Triphenyl phosphite and triphenylphosphine will reduce pyridine N-oxide at sufficiently high temperatures, ca. 200° ,^{122,126} but similar attempts to reduce 4-nitropyridine N-oxide resulted in evolution of nitrous fumes, and the fate of the remainder of the molecule was undetermined.¹²⁶

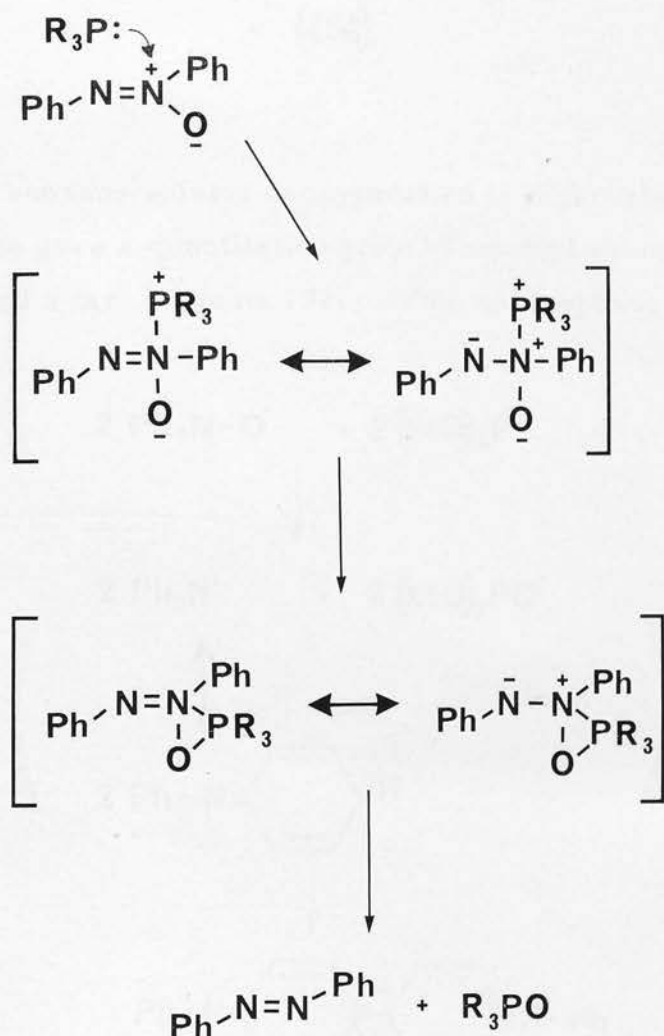
In addition, triethyl phosphite has been shown to reduce pyridine N-oxide at room temperature in the presence of oxygen and peroxides, but in this case the reducing species is more probably a peroxy-radical (231), as suggested by Emerson and Rees (scheme 135).¹²⁷



Scheme 135

Benzonitrile oxides can be reduced to the corresponding benzonitrile by treatment with triphenylphosphine or triethyl phosphite,¹²⁸ and, as discussed in section A. 2(a), benzofuroxan gives benzofurazan on treatment with triethyl phosphite.⁸ Cadogan³⁴ and Mukaiyama^{10b} and their co-workers have shown that azoxybenzene can be readily reduced to azobenzene by triethyl phosphite, but, under those conditions used to deoxygenate pyridine N-oxides, PCl_3 is unreactive towards azoxybenzene. Mukaiyama

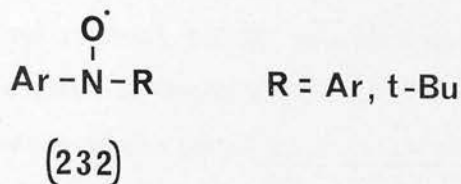
and his co-workers have described a mechanism to explain this result which involves initial nucleophilic attack by the phosphorus reagent at the quaternary nitrogen, but this leads to the intermediacy of an unlikely pentacovalent nitrogen species (scheme 136).



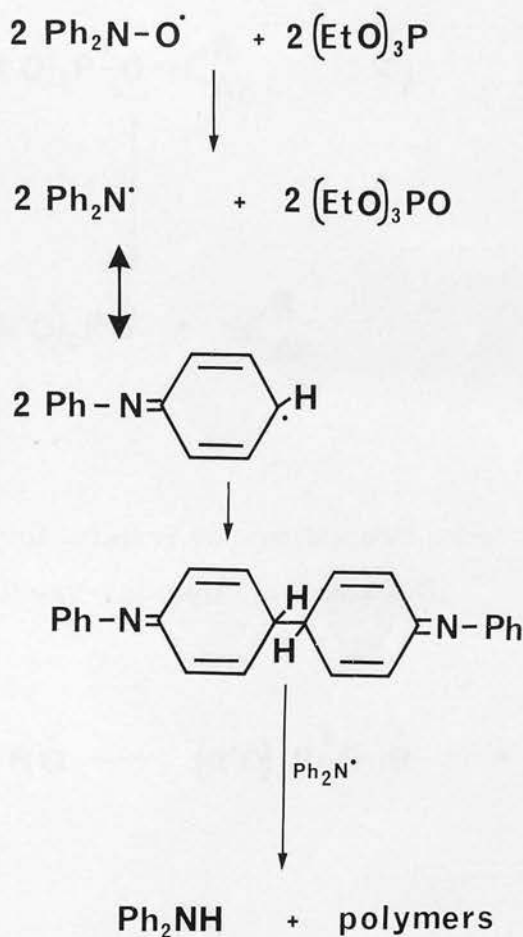
Scheme 136

C. 2 Deoxygenation of Nitroxyl Radicals

Cadogan and Rowley¹²⁹ have investigated the reaction of N-aryl nitroxyl radicals (232) with trialkyl phosphites and have provided evidence which shows that aminyl radicals are formed, in addition to the trialkyl phosphate.



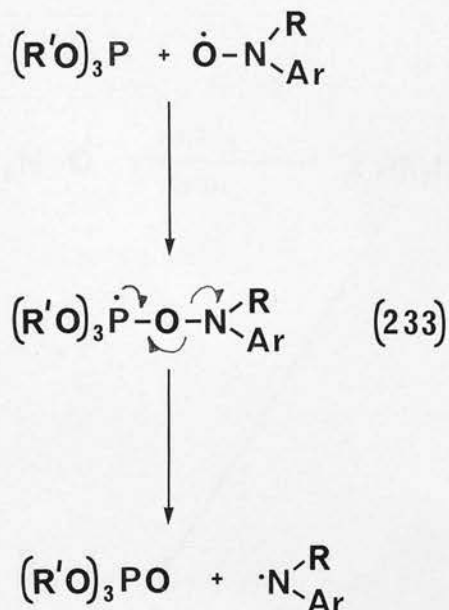
Thus in benzene solvent deoxygenation of diphenylnitroxyl by triethyl phosphite gave a quantitative yield of triethyl phosphate, diphenylamine (44%) and a tar (scheme 137). This corresponds closely to the known



Scheme 137

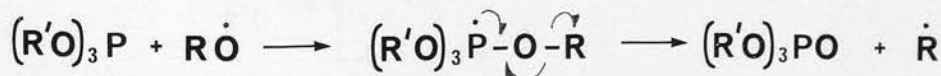
reaction¹³⁰ of diphenylaminyl radicals which may be generated by thermolysis of tetraphenylhydrazine.¹³¹

Cadogan and Rowley suggest that the deoxygenation of the nitroxyl radical occurs by addition of the radical to phosphorus, to give an intermediate phosphoranyl radical (233), in which the phosphorus atom has expanded its valence shell to include nine electrons. The reaction then proceeds by β -scission of the new ligand to give the phosphate and aminyl radical (scheme 138). Such a scheme is not unlikely in view of



Scheme 138

the behaviour of trialkyl phosphites with other radicals,^{6, 132} and in particular, alkoxy-radicals (scheme 139).¹³³ An alternative decom-

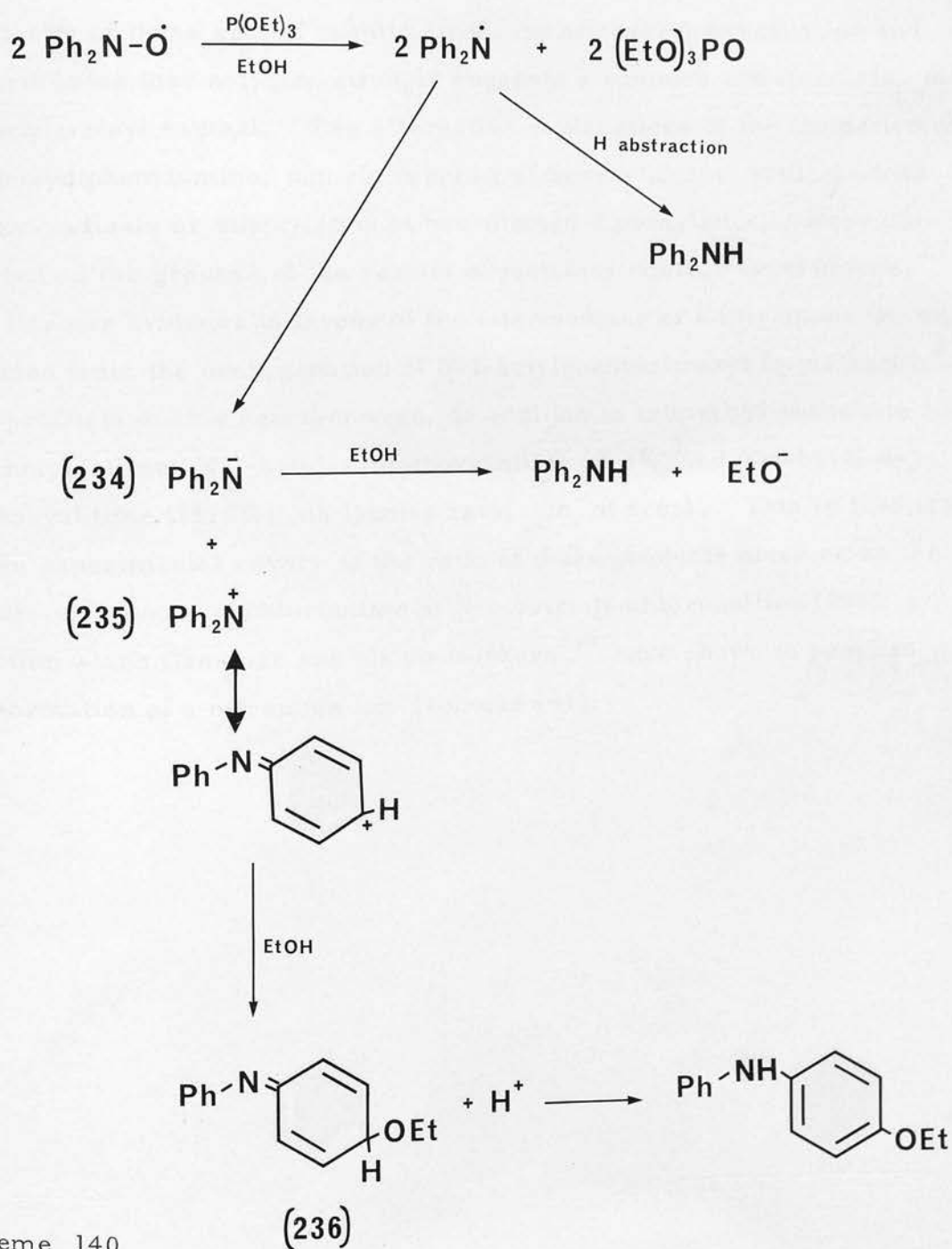


Scheme 139

position route for the phosphoranyl radical (233), involving β -scission of an alkoxy-ligand, is not observed, presumably because the resulting alkyl radical would be of higher energy than the delocalised aminyl radical.

Unexpected results, however, were obtained when the deoxygenation

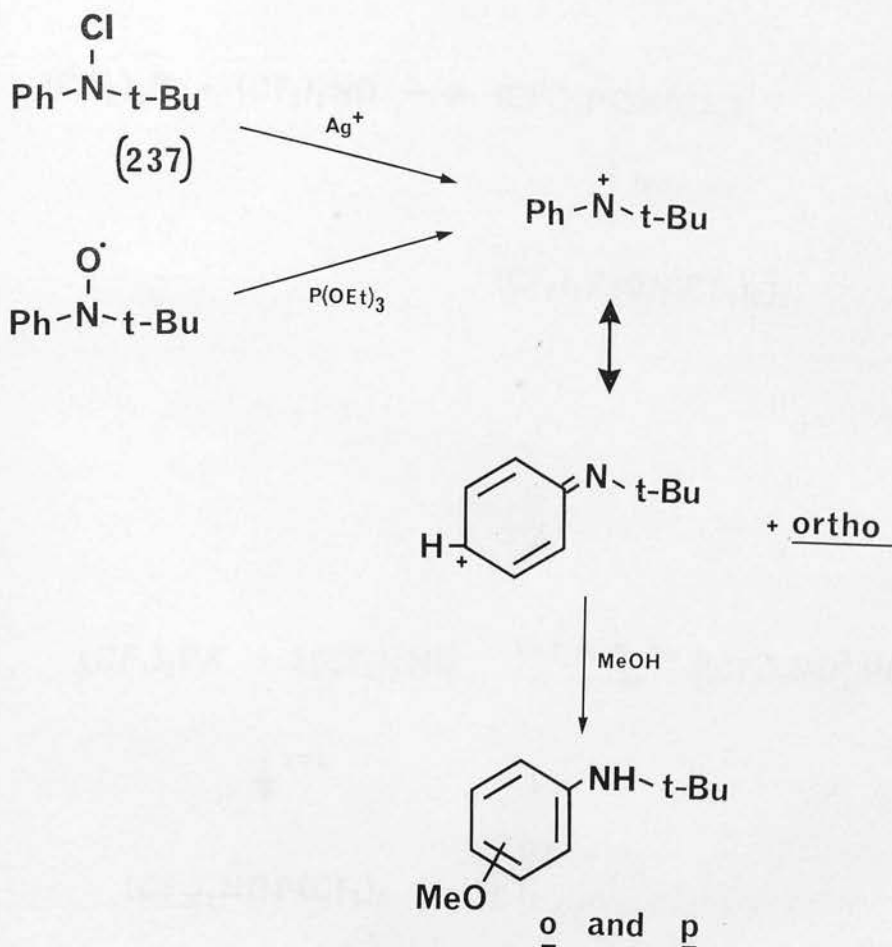
reactions were carried out in an alcohol solvent.¹²⁹ For example, after reaction of diphenylnitroxyl with triethyl phosphite in boiling ethanol the products were found to be triethyl phosphate (100%), diphenylamine (65%), and 4-ethoxydiphenylamine (19%). In order to explain the formation of the substituted diphenylamine Cadogan and Rowley proposed a mechanism involving electron transfer between aminyl radicals, to give a nitrogen anion (234) and a nitrenium ion (235) (scheme 140).



Scheme 140

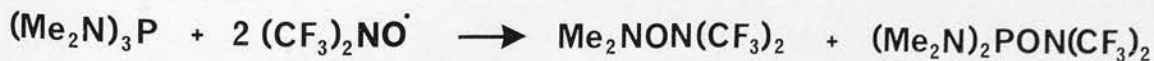
Diphenylamine arises from hydrogen abstraction by the diphenylaminyl radical and also by reaction of the anion (234) with the solvent. The nitrenium ion (235) would be expected to be stabilised by electron donation from each phenyl group, permitting nucleophilic attack by the solvent on the aromatic nucleus, as shown in the scheme. The quinone imine (236) would readily rearomatise via a hydrogen-shift to give the observed product, 4-ethoxydiphenylamine. Thermolysis, in ethanol, of tetraphenylhydrazine, an authentic source of diphenylaminyl radicals, was also found to give diphenylamine (67%) and 4-ethoxydiphenylamine (17%).¹²⁹ The close similarity of these sets of results, from the nitroxyl deoxygenation and the hydrazine thermolysis, strongly suggests a common intermediate, the diphenylaminyl radical. Two alternative explanations of the formation of 4-ethoxydiphenylamine, namely coupling of diphenylaminyl radicals with ethoxy-radicals or ethoxylation of pre-formed diphenylamine, were discounted on the grounds of the results of judicious control experiments.¹²⁹

Further evidence in favour of the intermediacy of a nitrenium ion was obtained from the deoxygenation of N-t-butylphenylnitroxyl in methanol.¹²⁹ The products of this reaction were, in addition to trimethyl phosphate and N-t-butylaniline, N-t-butyl-2-methoxyaniline (2.3%) and N-t-butyl-4-methoxyaniline (15.3%), an isomer ratio p:o of 6.6:1. This is identical, within experimental error, to the ratio of these products obtained by the silver-ion induced dechlorination of N-t-butyl-N-chloroaniline (237), a reaction which Gassman and his co-workers¹³⁴ have shown to proceed via the formation of a nitrenium ion (scheme 141).

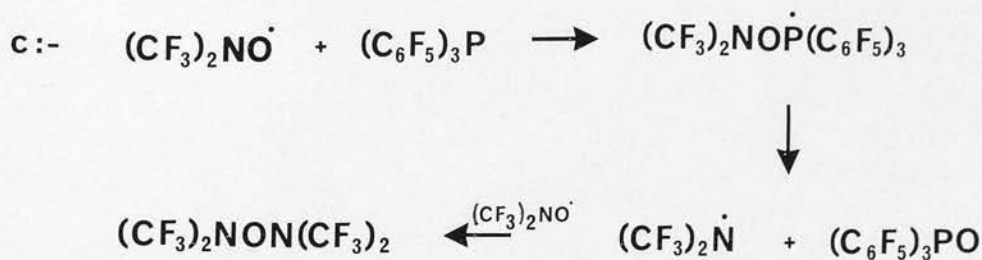
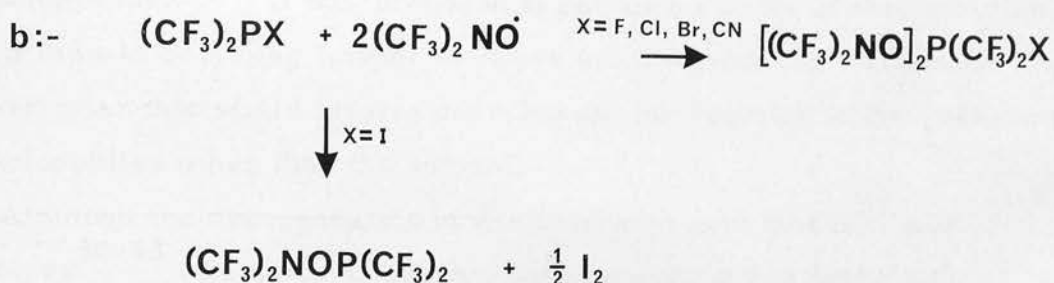
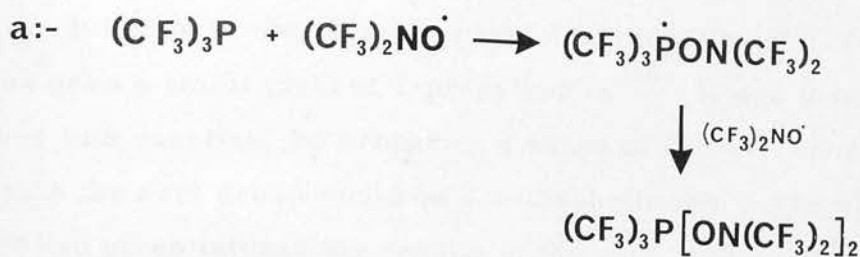


Scheme 141

Few other examples of the reaction between nitroxyl radicals and tervalent phosphorus reagents have been recorded. Nigumi and Emeleus¹³⁵ showed that the reaction of bis(trifluoromethyl)nitroxyl with tris(dimethylamino)phosphine proceeded as follows:



The reactions of a variety of perfluorinated phosphorus reagents with bis(trifluoromethyl)nitroxyl¹³⁶ gave pentavalent adducts, trivalent substitution products, or a phosphine oxide, depending on the starting reagent (scheme 142).



Scheme 142

A feature of the mechanism proposed by Ang and Lien^{136c} for the oxidation of $(\text{C}_6\text{F}_5)_3\text{P}$ (scheme 142, c) is β -scission of the nitroxyl ligand, in agreement with the mechanism of Cadogan and Rowley (scheme 138).

D. Programme of Research

It had been shown earlier that deoxygenation of 1, 2-diphenylnitroethene gave a small yield of 2-phenylindole.³⁴ It was decided to investigate further this reaction, by preparing a range of 2-aryl-1-phenylnitroethenes in which the aryl group would be 2, 6-disubstituted. The blocked-ortho effect had given interesting results in the past, and might be expected to alter the course of this reaction. In addition to examining the reaction products, it might prove possible to observe intermediate compounds by recording n. m. r. spectra during the course of the reaction.

The deoxygenation of nitroxyl radicals by triethyl phosphite in alcohol solutions had been shown to give alkoxy-anilines, possibly via nitrenium ions.¹²⁹ It was proposed to continue studies of this reaction with a view to obtaining further evidence for the proposed mechanism. In particular this would involve carrying out the reaction in the presence of nucleophiles other than the solvent.

Although the deoxygenation of 2-nitrophenyl aryl ethers⁵⁸ and sulphides⁵⁰⁻⁵³ was quite thoroughly documented, it was thought that further details of the effects of solvents and the thermal stability of products might be obtained by performing appropriate experiments.

Experimental

A. Instrumentation

Nuclear Magnetic Resonance Spectroscopy (n. m. r.). -

(a) Routine ^1H n. m. r. spectra were recorded on a Varian EM360 spectrometer. 100MHz spectra of new compounds were obtained using a Varian HA100 spectrometer operated by Mr. J. Miller. This instrument was also used in decoupling and variable temperature studies. Chemical shifts (δ) are measured in parts per million (p. p. m.) relative to tetramethylsilane (T. M. S.) as internal standard ($\delta = 0.0$).

(b) All ^{31}P n. m. r. spectra, including variable temperature studies, were recorded on a Varian XL100 spectrometer operated by Dr. A. Boyd. Unless otherwise stated the spectra were proton noise decoupled. Chemical shifts (δ) are measured in p. p. m. relative to external phosphoric acid (H_3PO_4 , 85%) ($\delta = 0.0$). Shifts to high frequency of the standard are positive.

(c) ^{13}C n. m. r. spectra were recorded on a Varian CFT20 spectrometer operated by Mr. J. Miller. Chemical shifts (δ) are measured in p. p. m. relative to internal T. M. S. ($\delta = 0.0$).

Infra-red Spectroscopy. - I. r spectra were recorded on a Perkin-Elmer 157G Grating Spectrophotometer. Liquid samples were recorded as thin films, and solid samples as nujol mulls.

Ultra-violet Spectroscopy. - U. v. spectra were recorded using a Unicam SP800 spectrophotometer. Solutions of samples were prepared in absolute ethanol.

Mass Spectroscopy. - An Associated Electrical Industries MS902 instrument, operated by Mr. D. Thomas, was used to obtain mass spectra and exact masses.

Elemental Analysis. - Mr. J. Grunbaum of the University of Edinburgh carried out all elemental analyses of new compounds using a Perkin-Elmer model 240 analyser.

Melting Points:- Routine melting points were obtained using open capillary tubes and Gallenkamp apparatus. Melting points of new compounds were obtained using a Kofler hot-stage apparatus.

Gas-liquid Chromatography (g.l.c.).- A Pye Series 104 chromatograph with a flame ionisation detector was used in analytical investigations. Columns were 2m x 4 mm i. d. and the carrier gas was nitrogen. The stationary phase was OV225 or PEG1500 supported on silanised Chromasorb W, or 5% KOH-washed celite, respectively.

Quantitative analysis was performed by the internal standard method with the aid of a Spectra-Physics Autolab minigrator. The detector response was calibrated for each compound in the reaction mixture by analysis of a known mixture of authentic samples. Biphenyl, generally employed as the internal standard, was purified by chromatography on alumina.

Several analytical investigations were also carried out using a Pye Series 104 chromatograph coupled to a Micromass 12 mass spectrometer operated by Dr. P. Bell.

Preparative g.l.c. was carried out using a Pye Series 105 preparative chromatograph. The column, 4.6m x 10mm o. d. , was packed with 10% PEG 1500 supported on 5% KOH-washed celite.

High Pressure Liquid Chromatography (h.p.l.c.).- Analytical investigations by h.p.l.c. were carried out using 0.5 cm diameter polished stainless steel columns¹³⁷ slurry-packed with 5 micron Spherisorb silica, and coupled to a Cecil Instruments CE12 UV monitor, set at 254nm, which served as detector. The mobile phase was hexane, 50% water-saturated, containing a small percentage of dioxan, ethyl acetate, or dichloromethane. Further details of this technique are published elsewhere.^{50d, 57}

Medium Pressure Liquid Chromatography. - Preparative chromatography using pressurised eluants was carried out in glass columns and fittings supplied by Jobling. The column packing was 50 micron silica. A u.v. detector by Laboratory Data Control was used to monitor the output from the column to the fraction collector.

Thin Layer Chromatography (t.l.c.). - Chromatograms were developed on 0.33 mm layers of alumina (Merck, Aluminium Oxide G) or silica gel (Merck, silica gel G), containing Woelm fluorescent green indicator (0.5%). Components of the chromatogram were detected by their quenching of fluorescence under u.v. light.

B. Preparation of Materials

B.1 General Reagents. - Benzene, t-butylbenzene, cumene and decalin were dried over sodium wire, redistilled, and stored over molecular sieve. Petrol ether was redistilled. "Dry ether" was prepared by treating commercially available anhydrous diethyl ether with sodium wire. Ethanol and methanol were dried by distillation from activated magnesium and stored over molecular sieve. Where necessary, solutions in ether, benzene, or halogenated solvents were dried over anhydrous magnesium sulphate.

Triethyl phosphite and trimethyl phosphite were dried over sodium wire and redistilled before use. Dimethylphenylphosphonite and 2-phenyl-1,3,2-dioxaphospholan were prepared by the generally reported method of treating dichlorophenylphosphine with methanol and 1,2-ethanediol respectively in the presence of a tertiary amine, followed by redistillation prior to use.

Nitrogen was British Oxygen white spot, dried by passing successively through concentrated sulphuric acid and potassium hydroxide pellets.

Except for specific compounds described in the following sections, all other reagents were commercially available and, where appropriate, were recrystallised or redistilled before use.

B.2 2-Aryl-1-phenylnitroethenes. - E-2-Aryl-1-phenylnitroethenes were prepared by the method of Robertson,¹³⁸ as exemplified by the preparation of E-2-(2,4,6-trimethoxyphenyl)-1-phenylnitroethene.

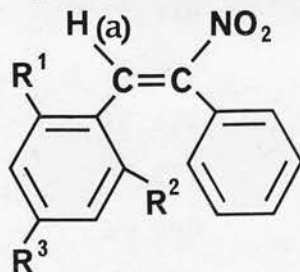
A solution of 2,4,6-trimethoxybenzaldehyde (19.6 g, 0.1 mole) and n-butylamine (7.3 g, 0.1 mole), in benzene (50 ml), was boiled under reflux in a flask

fitted with a Dean and Stark water trap. After about 30 min, when 1.8 ml of water had been separated, the benzene was removed by distillation to leave the Schiff's base. Without further purification this was added to a solution of phenylnitromethane¹³⁹ (13.7 g, 0.1 mole) in glacial acetic acid (25 ml). After standing at room temperature for 5 days the solution was poured into 25 ml of water and the oil which separated was collected. Crystallisation of the oil was induced by scratching. In subsequent preparations the acetic acid solution was seeded with a crystal of the compound, and after 24 h the yellow solid was filtered off. Recrystallisation from ethanol afforded the required product (12.3 g, 0.039 moles, 39%), m. p. 165-166^o. (Found: C, 64.8; H, 5.4; N, 4.4. $C_{17}H_{17}NO_5$ requires C, 64.8; H, 5.4; N, 4.4%; δ (CDCl₃) 3.42 (6H, s), 3.78 (3H, s), 5.96 (2H, s), 7.24 (5H, m), 8.21 (1H, s).

Other nitroethenes, all known compounds, which were prepared by this method are given in Table 1.

TABLE 1

E-2-Aryl-1-phenylnitroethenes



| Compound | R ¹ | R ² | R ³ | Yield | m. p. | (Lit ¹³⁸ m.p.) |
|----------|-------------------|-------------------|-------------------|-------|------------------------|-----------------------------|
| A | H | H | H | 60% | 69-70 ^o | (73-74 ^o) |
| B | CH ₃ | CH ₃ | CH ₃ | 74% | 113-115 ^o | (115-116 ^o) |
| C | Cl | Cl | H | 87% | 133-134.5 ^o | (136-136.5 ^o) |
| D | NO ₂ | H | H | 66% | 95-98 ^o | (101.5-102.5 ^o) |
| E | CH ₃ O | CH ₃ O | CH ₃ O | 39% | 165-166 ^o | (-) |

Attempts to prepare 2-(2-pyridyl)-1-phenylnitroethene and 2-(2-pyrrolyl)-1-phenylnitroethene by the above method failed.

The E-configuration of the nitroethenes (aryl groups cis) was determined in the first instance for 1,2-diphenylnitroethene (α -nitrostilbene) by Freeman and Stevens,¹⁴⁰ by analysis of the u. v. absorption spectrum. The E-configuration of the substituted 1,2-diphenylnitroethenes in Table 1 was confirmed by comparisons of the u. v. spectra and the chemical shifts, δ (Ha), of the olefinic hydrogens. These data are given in Table 2, together with the corresponding data for Z-1,2-diphenylnitroethene (see below).

TABLE 2

2-Aryl-1-phenylnitroethenes: u. v. absorption spectra and chemical shifts, δ (Ha), of olefinic hydrogens.

| <u>Compound</u> ^{a)} | <u>λ_{\max}</u> | <u>ϵ_{\max}</u> | <u>δ (Ha)</u> |
|-------------------------------|------------------------------------|-------------------------------------|---------------------------------|
| A | 312 | 12,039 | 8.15 |
| | 273 | 10,932 | |
| | 266 | 11,748 | |
| | 260 | 10,000 | |
| | 233 | 12,621 | |
| B | 325 | 5,217 | 8.04 |
| | 250 | 10,000 | |
| C | 284 | 4,120 | 7.82 |
| | 272 | 4,387 | |
| | 265 | 4,465 | |
| | 252 | 4,748 | |
| D | 321 | 4,945 | 8.43 |
| | 264 | 11,538 | |
| | 231 | 15,934 | |
| E | 372 | 7,457 | 8.20 |
| | 285 | 8,924 | |
| | 263 | 8,802 | |
| | 226 | 16,626 | |
| F ^{b)} | 281 ^{c)} | 21,500 ^{c)} | 6.80 |

- a) Compounds lettered as in Table 1.
- b) Z-1,2-Diphenylnitroethene.
- c) Results of Freeman and Stevens.¹⁴⁰

Z-1,2-Diphenylnitroethene. - A solution of E-1,2-diphenylnitroethene (10 g) in ethanol (250 ml) was irradiated for 5 h using a 400 W medium pressure Hg lamp with pyrex filter. The volume of solvent was reduced by 50% and the precipitated solid was collected and recrystallised from methanol to give the required compound (2.73 g, 27%), m. p. 124-126° (lit¹⁴⁰ 127-128°).

1,2,2-Triphenylnitroethene.¹⁴¹ - A solution of 1,2-diphenylnitroethene (10 g, 0.045 moles) in dry ether (50 ml) was added dropwise to phenyl magnesium bromide (0.081 mole) in dry ether (50 ml) and the resulting solution was boiled for 15 min. The solution was then cooled in an ice-salt bath and bromine (13.0 g, 0.081 mole) was added dropwise with vigorous stirring. When the addition was complete, stirring was continued for a further 30 min as the temperature rose to room temperature. The grey precipitate was filtered off and washed with water and ether. Recrystallisation from acetone gave α -bromo- α -nitro- α,β,β -triphenylethane (3.66 g, 0.0096 moles, 21%), m. p. 182° dec. The bromo-compound was then added to sodium methoxide solution (1.15 g Na in 25 ml of methanol) and the suspension was stirred and boiled for 1 h. The yellow precipitate was filtered off, washed with water and methanol, and recrystallised from acetone to give 1,2,2-triphenylnitroethene (1.55 g, 0.0051 moles, 11.3% overall), m. p. 173-177° (lit¹⁴¹ 170°).

A sample of 2-(2-furyl)-1-phenylnitroethene was kindly provided by Professor J. I. G. Cadogan.

B.3 Aryl 2-nitrophenyl sulphides and ethers

2,6-Dichlorophenyl 2'-nitrophenyl sulphide. - This was prepared by the method of Galt and Loudon,¹⁴² Aqueous sodium hydroxide (2 g NaOH in 2 ml H₂O) was added dropwise, with stirring, to a solution of 2,6-dichlorothiophenol (9 g, 0.05 mole) and 2-chloronitrobenzene (7.8 g, 0.05 mole) in ethanol (20 ml). The solution was then boiled under reflux for 1 h, cooled, and the yellow precipitate filtered off. Recrystallisation from ethanol gave 2,6-dichlorophenyl 2'-nitrophenyl sulphide (6.5 g, 0.022 mole, 43%), m.p. 122-123.5° (lit⁵¹ 123°).

2-Nitrophenyl phenyl ether. - This was prepared by the method of Wright and Jorgensen.¹⁴³ Phenol (16.9 g, 0.18 mole) and 2-chloronitrobenzene (23.7 g, 0.15 mole) were heated together at 95° with KOH (8.4 g, 0.15 mole) and dimethyl sulphoxide (200 ml) for 24 h under an atmosphere of nitrogen. The reaction mixture was then cooled and poured into 2N HCl (300 ml) and ice (100 g). After a thorough stirring, the brown oil was separated and distilled to give light yellow 2-nitrophenyl phenyl ether (20.3 g, 0.094 mole, 63%), b.p. 107-110°, 0.1 mmHg (lit¹⁴⁴ 183-185°, 8 mmHg). Also prepared in this way was 2,6-dimethyl-4-methoxyphenyl 2'-nitrophenyl ether (0.11 g, 0.40 mM, 29%), m.p. 116-116.5°. (Found: C, 64.6; H, 5.5; N, 5.0. C₁₅H₁₅NO₄ requires C, 65.9; H, 5.5; N, 5.1%).

2,6-Dichlorophenyl 2'-nitrophenyl ether. - This was prepared by a modification of the technique of Henley¹⁴⁵ devised by Dr. G. Abbot. Potassium hydroxide (7.5 g, 0.13 mole) and water (0.2 ml) were fused, then 2,6-dichlorophenol (26 g, 0.16 mole) was added and the mixture was heated to give a homogeneous liquid. 2-Chloronitrobenzene (15.8 g, 0.1 mole) was added and the mixture was heated at 210-220° for 1 h. After the mixture had been cooled and shaken with aqueous KOH a solid (22.3 g) was collected. After chromatography on alumina pale yellow crystals of 2,6-dichlorophenyl 2'-nitrophenyl ether were obtained (4.64 g, 0.017 mole, 16.8%), m.p. 114-115.5°. (Found: C, 51.0; H, 2.5; N, 4.75. C₁₂H₇Cl₂NO₃ requires C, 50.7; H, 2.5; N, 4.9%).

Several attempts were made to prepare 2,6-di-t-butylphenyl 2'-nitrophenyl ether and 2'-nitrophenyl 2,4,6-tri-t-butylphenyl ether. The following methods were employed without success: reaction of di- or tri-t-butylphenol with 2-chloronitrobenzene and base in DMSO,¹⁴³ hexamethylphosphoramide, or a trace of water;¹⁴⁵ reaction of the substituted phenol with 2-chloronitrobenzene under phase-transfer conditions;¹⁴⁶ Friedel-Crafts t-butylation of 2-nitrophenyl phenyl ether; reaction of the substituted phenol with 2-nitrodiphenyliodonium bromide.

The reaction of anthrone with 2-chloronitrobenzene in the presence of base failed to give 9-anthranyl 2'-nitrophenyl ether. Reactions of 9-bromoanthracene and 9-bromophenanthrene with sodium *o*-nitrophenoxide, *o*-nitrophenol, and copper, under high pressure conditions (an extension of a synthesis of 9-phenanthryl phenyl ether devised by Wittig and his co-workers¹⁴⁷) resulted in explosions.

Attempts to prepare 2,6-dicarboxyphenyl 2'-nitrophenyl ether by permanganate or chromate oxidation of 2,6-dimethylphenyl 2'-nitrophenyl ether gave only unreacted starting material.

The following compounds were prepared by Dr. P.K.K. Lim by the method of Wright and Jorgensen:¹⁴³ 4-chlorophenyl 2'-nitrophenyl ether, 2,6-dimethylphenyl 2'-nitrophenyl ether, 2,6-dimethoxyphenyl 2'-nitrophenyl ether, and 2-nitrophenyl 2',4',6'-trimethylphenyl ether.

B.4 Aryl 2-azidophenyl sulphides and ethers

These compounds were prepared from the corresponding 2-amino-compounds which were, in turn, prepared from 2-nitrophenyl aryl ethers or sulphides. For example, to a stirred mixture of 2,6-dichlorophenyl 2'-nitrophenyl ether (0.9 g, 0.003 mole), iron powder (1.1 g, 0.019 mole), ethanol (16 ml) and water (16 ml), was added concentrated hydrochloric acid (1 ml). The mixture was stirred and boiled under reflux, under nitrogen, for 16 h, before being made slightly basic by addition of 2N NaOH solution. The ethanol was distilled out of the mixture and the residue shaken with chloroform. The two layers were filtered through Celite and then separated. The organic layer was evaporated and the

residue was sublimed and recrystallised to give 2-aminophenyl 2',6'-dichlorophenyl ether (0.28 g, 0.0011 mole, 34%), m.p. 80-82°. (Found: C, 56.7; H, 3.6; N, 5.5. $C_{12}H_9Cl_2NO$ requires C, 56.7; H, 3.6; N, 5.5%). This amine (2.5 g, 0.0099 mole) was dissolved in 5N HCl (10 ml) and diazotised by addition, at 0°, of a solution of sodium nitrite (0.87 g, 0.013 mole) in water (3.5 ml). The solution was stirred for a further 2 h at 0° before a solution of sodium azide (1.63 g, 0.025 mole) in water (40 ml) was added slowly, and the temperature kept below 3°. The precipitate was collected, washed with water, and dried at room temperature in vacuo to give a light brown powder, 2-azidophenyl 2',6'-dichlorophenyl ether (2.1 g, 0.0075 mole, 76%), m.p. 76-77°. (Found: C, 51.3; H, 2.5; N, 14.9. $C_{12}H_7Cl_2N_3O$ requires C, 51.45; H, 2.5; N, 15.0%). Both of these compounds, the amine and the azide, showed the expected spectral characteristics. They were prepared in the first instance by Dr. G. Abbot. Similar methods were employed to prepare 2-amino- and 2-azidophenyl 2',6'-dimethoxyphenyl ether,¹⁴⁸ 2-amino- and 2-azidophenyl 4'-chlorophenyl ether,¹⁴⁸ and 2-amino- and 2-azidophenyl 2',6'-dichlorophenyl sulphide.^{50c, 51} The last compound was prepared by Dr. S. Kulik. Dr. P. K. K. Lim prepared 2,6-dimethyl- and 2,4,6-trimethylphenyl 2'-azidophenyl ethers.¹⁴⁸

B.5 N-Aryl-N-t-butyl (or-N-phenyl)hydroxylamines and nitroxyls.

t-Nitrosobutane and nitrosobenzene were prepared by standard literature methods,^{149, 150} and then reacted with an aryl magnesium bromide to give a hydroxylamine. For example, a solution of phenyl magnesium bromide (0.12 mole, theoretical) prepared in the usual way in dry ether, was cooled to -15° and a solution of nitroso-t-butyl (4.6 g, 0.053 mole) in dry ether (100 ml) was added dropwise over 75 min. The solution was stirred for a further 45 min and stood at room temperature overnight before being poured onto ice-cold water with vigorous stirring. The ether layer was separated and combined with further ether washings. The organic solution was dried, filtered, and evaporated to give a solid which was then recrystallised from petrol containing a few percent methanol, to give white crystals of N-t-butyl-N-phenylhydroxylamine (4.90 g, 0.03

mole, 56%), m. p. 115-118° (lit¹⁵¹ 116-117°). This method was also used to prepare N-t-butyl-N-(p-methylphenyl)hydroxylamine (45%), m. p. 121-123° (lit¹⁵¹ 121-122°), and N-t-butyl-N-(p-ethoxyphenyl)hydroxylamine (44%), m. p. 109.5-111.° (Found: C, 68.9; H, 9.3; N, 6.6. $C_{12}H_{19}NO_2$ requires C, 68.9; H, 9.15; N, 6.7%). All these compounds exhibited the expected spectral characteristics. The same general method, but with nitrosobenzene replacing nitroso-t-butyl, was used to prepare N, N-diphenylhydroxylamine¹⁵² (23%), which was used immediately in the preparation of the nitroxyl.

Oxidation of the hydroxylamines to the corresponding nitroxyls was effected by treatment with silver oxide.^{153, 154} For example, N, N-diphenylhydroxylamine (8.4 g, 0.045 mole) was dissolved in dry ether (50 ml) and cooled to 0°. Silver oxide, Ag_2O , (10.4 g, 0.045 mole) was added, and the mixture was stirred vigorously for 10 minutes. The red solution was filtered and the ether was evaporated at room temperature. The residue was stirred with 100 ml of petrol, and the solution decanted from the black tar. This was repeated and the combined petrol washings were cooled to -78° to precipitate crystalline N, N-diphenylnitroxyl, which was rapidly collected and dried in a vacuum desiccator (2.1 g, 0.011 mole, 25%), m. p. 52-56° (lit¹⁵³ 62°). In a similar manner N-t-butyl-N-phenylnitroxyl and N-t-butyl-N-(p-methylphenyl)nitroxyl were prepared as red oils¹⁵⁴ which were used directly in the deoxygenation reactions (see Section H).

B.6 Tetraz-2-enes

The N-nitrosation of an aniline and subsequent reduction of the N-nitroso-compound to give a hydrazine, followed by oxidative coupling, gave a tetraz-2-ene.¹⁵⁵ For example, a solution of sodium nitrite (11.4 g, 0.17 mole) in water (40 ml) was added to a suspension of N-t-butylaniline (7.6 g, 0.051 mole) in concentrated HCl (20 ml) and ice (50 g). The mixture was stirred for 2 h at 0°, the product filtered off and recrystallised from ethanol to give N-t-butyl-N-nitrosoaniline (5.8 g, 0.033 mole, 65%), m. p. 58-60° (lit¹⁵⁵ 60-62°). A solution of N-t-butyl-N-nitrosoaniline (5.8 g, 0.033 mole) in acetic acid (14 ml) and

water (14 ml) was stirred with zinc dust (50 g, 0.76 mole), keeping the temperature below 10° . The zinc dust had been previously activated by washing with 2% HCl (2 x 150 ml), water (3 x 150 ml), ethanol (2 x 100 ml) and dry ether (100 ml). After 2 h, the reaction mixture was filtered and the cake was washed with 5% HCl (3 x 10 ml). The combined filtrate was basified by addition of 20% NaOH solution (100 ml), and extracted with ether (3 x 100 ml). The combined extracts were dried and the solvent evaporated to give an oil (5.0 g) which contained N-t-butyl-aniline and N-t-butyl-N-phenylhydrazine. Examination of the ^1H n.m.r. spectrum of the oil enabled the yield of hydrazine to be determined as approximately 60%. The oil containing N-t-butyl-N-phenylhydrazine (0.020 mole approx) was dissolved in ethanol (60 ml) and the solution cooled to -10° , before being added to a similarly cooled solution of quinone (2.4 g, 0.022 mole) in ethanol (100 ml). The combined solution was stirred at -10° for 2 h, then the solvent was evaporated under high vacuum. The residue was washed with cold (-20°) ethanol (10 ml), giving pale yellow crystals. Recrystallisation from ethanol at -78° gave 1,4-di-t-butyl-1,4-bis(phenyl)tetraz-2-ene (2.1 g, 0.006 mole, 60%), m.p. $115-117^{\circ}$ dec (lit¹⁵⁵ $130-131^{\circ}$ dec). (Found: C, 74.1; H, 8.9; N, 17.0. Calc. for $\text{C}_{20}\text{H}_{28}\text{N}_4$: C, 74.0; H, 8.7; N, 17.3%). The same method was used to convert N-methylaniline into 1,4-dimethyl-1,4-bis(phenyl)tetraz-2-ene which was purified by chromatography on an alumina column and recrystallisation from ethanol at -78° (1.3 g, 0.0054 mole, 14%) m.p. $140-143^{\circ}$ dec (lit 133° ¹⁵⁶, $139-140^{\circ}$ ¹⁵⁷).

B.7 Authentic samples of reaction products

N-t-Butylaniline was prepared by reduction of N-t-butyl-N-phenylhydroxylamine. The hydroxylamine (20 g, 0.12 mole) was dissolved in 5N hydrochloric acid (250 ml), tin granules (40 g, 0.34 mole) were added, and the solution was stirred for 16 h. The solution was basified (NaOH) and filtered through Celite. The reaction flask and filter cake were washed with ether (500 ml). The ether solution was dried and evaporated to give a pale yellow oil which was distilled to give pure N-t-butylaniline (15.7 g, 0.105 mole, 88%), b.p. $86.5-87.5^{\circ}$, 11 mmHg

(lit¹⁵⁸ 92.5-98°, 19.5 mmHg). In the same way reduction of N-t-butyl-N-(p-ethoxyphenyl)hydroxylamine gave N-t-butyl-p-ethoxyaniline (2.86 g, 0.0148 mole, 78%), $n^{20.5}_D = 1.5127$. The hydrochloride derivative was analysed. (Found: C, 62.1; H, 8.75; N, 5.8. $C_{12}H_{20}ClNO$ requires C, 62.7; H, 8.7; N, 6.1%).

N-t-Butyl-o- and p-chloroanilines were prepared by reacting N-t-butylaniline (4.9 g, 0.03 mole) with N-chlorosuccinimide (4.4 g, 0.03 mole) in boiling benzene for 100 min. After cooling, filtration and evaporation, the residue was added to 6N sodium hydroxide solution (100 ml) and steam distilled. Extraction of the distillate with ether followed by evaporation of the extracts gave a dark green oil which was shown, by g.l.c., to consist of N-t-butyl-o- and p-chloroaniline, plus a trace of N-t-butyl-2,4-dichloroaniline. Mass spectra obtained by the g.l.c.-m.s. technique confirmed the structures of the compounds. Small quantities of the pure compounds, sufficient for the determination of the sensitivity factors for a flame-ionisation detector, were obtained by preparative g.l.c.

p-Chlorodiphenylamine was prepared by the combined methods of Allen and McKee,¹⁵⁹ and Massie and Kabada.¹⁶⁰ p-Chloroaniline (52.1 g, 0.41 mole) was melted and potassium carbonate (anhyd, 16 g) and copper bronze (0.4 g) were added. o-Chlorobenzoic acid (16.0 g, 0.10 mole) was then added in portions with stirring. Stirring was continued for 2 h, with the temperature maintained at 185°. The crude mixture was then steam distilled, and the brown residual solution was boiled with decolourising charcoal. After removal of the charcoal, the filtrate was acidified to precipitate pale green, impure N-(p-chlorophenyl)-anthranilic acid (13.1 g, 0.055 mole, 54%), m.p. 163-166° (lit¹⁶¹ 177°). This compound (3.0 g, 0.013 mole) was heated at 240° for 2 h. The residue was purified by column chromatography on alumina to give pink crystals which were recrystallised from benzene; p-chlorodiphenylamine (1.3 g, 0.0064 mole, 51%), m.p. 68-70° (lit¹⁶² 74°). (Found: C, 70.5; H, 5.0; N, 6.8. Calc. for $C_{12}H_{10}ClN$: C, 70.8; H, 4.95; N, 6.9%).

In a similar manner p-anisidine and o-chlorobenzoic acid gave N-(p-methoxyphenyl)anthranilic acid (2.60 g, 0.011 mole, 30%), m.p.

181-184° (lit¹⁶³ 186°), which subsequently gave *p*-methoxydiphenylamine (0.95 g, 4.8 mM, 58%), m. p. 105-105.5° (lit¹⁶⁴ 105°).

Authentic samples of 2-phenylindole, 5,11-dihydro-4-methyl-dibenzo[*b*, *e*][1,4]oxazepine, 5,11-dihydro-2,4-dimethyldibenzo[*b*, *e*][1,4]-oxazepine, 4-methoxyphenoxazine, 1,2-dimethoxyphenoxazine, 1-chlorophenothiazine, and 4-chlorophenothiazine were kindly provided by Professor J. I. G. Cadogan.

B. 8 Miscellaneous compounds

2-Chlorocyclohexyl 2'-nitrophenyl sulphide. - A solution, in ether (150 ml), of cyclohexene (18.9 g, 0.23 mole) and *o*-nitrobenzenesulphenyl chloride (19 g, 0.1 mole), which was prepared by the method of Hubacher,¹⁶⁵ was boiled under reflux for 20 h. Most of the ether was then removed by evaporation and the precipitated product, 2-chlorocyclohexyl 2'-nitrophenyl sulphide, was collected and recrystallised from ethanol to give bright yellow prisms (24.6 g, 0.091 mole, 91%), m. p. 99.5-100° (lit¹⁶⁶ 100-102°). Attempts to dehydrohalogenate this compound with triethylamine and aqueous KOH were unsuccessful.

2-(1,1-Diphenylethenyl) 2'-nitrophenyl sulphide. - A solution of 1,1-diphenylethylene (2.2 g, 0.012 mole) and *o*-nitrobenzenesulphenyl chloride (1.9 g, 0.01 mole) in tetrahydrofuran was allowed to stand at room temperature for 40 h. The solvent was removed by evaporation and the residue was dissolved in CH₂Cl₂ and eluted on an alumina column. A distinct yellow band was collected, and removal of solvent gave an oil which crystallised on cooling. Recrystallisation from ethanol gave 2-(1,1-diphenylethenyl) 2'-nitrophenyl sulphide (2.33 g, 0.007 mole, 70%), m. p. 88-90.5°. (Found: C, 71.9; H, 4.5; N, 4.3. C₂₀H₁₅NO₂S requires C, 72.1; H, 4.5; N, 4.2%).

2,6-Dimethyl-4-methoxyphenol. - 2,6-Dimethylquinone, prepared by the methods of Noelting and Baumann¹⁶⁷ or Smith *et al*,¹⁶⁸ was reduced to 2,6-dimethylquinol with zinc powder and acetic acid. The quinol (0.71 g, 5.1mM) was dissolved in methanol (25 ml), and concentrated sulphuric

acid (5 ml) was added dropwise to the solution. After the solution had been boiled for 30 min, dilution with water gave a crystalline precipitate of 2,6-dimethyl-4-methoxyphenol (0.29 g, 1.9mM, 37%), m. p. 70-71^o (lit¹⁵⁸ 77^o).

2-Nitrodiphenyliodonium bromide. - o-Nitroiodosobenzene (33 g, 0.125 mole), prepared by the method of Lucas et al,¹⁶⁹ was added in portions, over 25 min, to a mixture of conc. H₂SO₄ (150 ml) and benzene (22 ml) which was kept at 5^o. The mixture was then stirred for 4 h, at room temperature, after which 1 kg of ice and 8.5 g of Celite were added. The solution was filtered and sodium bromide (21 g dissolved in 10 ml of water) was added. The yellow precipitate was collected, washed with water, methanol and dry ether, and dried in air to give 2-nitrophenyliodonium bromide (41.6 g, 0.102 mole, 82%), m. p. 136-137^o (lit¹⁷⁰ 143^o dec).

Sodium 2-nitrophenoxide. - Sodium (3.4 g, 0.15 mole) was dissolved in ethanol (500 ml), 2-nitrophenol (20.5 g, 0.15 mole) was added, and the solution was stirred for 1 h. Removal of the ethanol in vacuo gave a bright red solid, sodium 2-nitrophenoxide (22.2 g, 0.13 mole, 93%), m. p. >325^o.

Benzyl-tri-n-butylammonium bromide. - Benzyl bromide (71.5 g, 0.42 mole) and tri-n-butylamine (77.7 g, 0.42 mole) were dissolved in benzene (400 ml) and the solution was boiled under reflux for 5 h. After cooling the white crystalline product was filtered off and dried; benzyl-tri-n-butylammonium bromide (128 g, 0.358 mole, 87%).

C. Deoxygenation of 2-Aryl-1-phenylnitroethenes

General method. - To the 2-aryl-1-phenylnitroethene, or to a solution of the 2-aryl-1-phenylnitroethene, was added the tervalent phosphorus reagent, usually in a two-fold stoichiometric excess. Oxygen was eliminated by bubbling nitrogen through the solution for 5-10 min. The solution was then boiled under reflux in an atmosphere of nitrogen

for the stated time, and subsequently the solvent, together with as much of the phosphate and excess phosphite as possible, was removed by distillation under reduced pressure. Column chromatography on alumina or silica, generally with ether:petrol mixtures as eluants, was used to separate products from the residue. A general feature of the reactions was the poor accountancy of materials after chromatography. Although washing of the columns with a highly polar solvent such as ethanol gave small amounts of intractable oils, it must be assumed that a proportion of each reaction residue was strongly absorbed by the column packing.

1) E-1, 2-Diphenylnitroethene. - Deoxygenation by triethyl phosphite:

(i) the reaction was carried out in the absence of solvent for 16 h, by the general method. In addition to trace amounts of unidentified materials, 2-phenylindole (0.076 g, 0.39 mmole, 8%), m. p. 181-184 (lit³⁴ 188-189°) was obtained. Identification was confirmed by comparisons of i. r. and n. m. r. spectra with those of an authentic sample. Triethyl phosphate (75%) was also isolated.

(ii) The nitroethene (1.13 g, 0.005 mole) and triethyl phosphite (2.82 g, 0.017 mole) were dissolved in decalin (25 ml). After reaction at the boiling point for 3.5-4 h, chromatography gave 2-phenylindole (0.18 g, 0.93 mmole, 18%), identified by comparison with an authentic sample.

(iii) A solution of the nitroethene (2.25 g, 0.01 mole) and triethyl phosphite (6.65 g, 0.04 mole) in cumene (50 ml) was boiled for 54 h. Chromatography gave a dark green oil (0.53 g) which on sublimation gave white crystals of deoxybenzoin (0.20 g, 0.001 mole, 10%), m. p. 50-54° (lit¹⁷¹ 60°), identified by its mass spectrum and comparison of i. r. spectrum with published data.¹⁷² Intractable oils and pastes were also obtained.

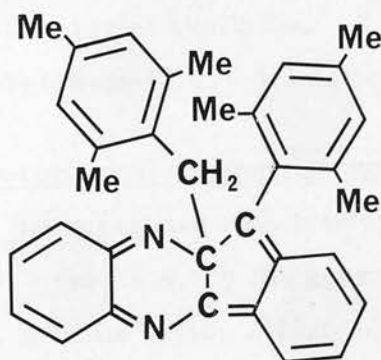
(iv) The nitroethene (2.25 g, 0.01 mole) and triethyl phosphite (6.7 g, 0.04 mole) were dissolved in benzene and heated at the boiling point for 42 h. T. l. c. examination showed that all the nitroethene had reacted, but only small amounts of unidentified oils and 0.08 g of a brown powder, m. p. ca 173-200°, were obtained.

Deoxygenation of E-1, 2-diphenylnitroethene by trimethyl phosphite, in benzene or decalin, or without solvent, gave no single product, other than trimethyl phosphate, in isolable yield.

2) Z-1, 2-Diphenylnitroethene. - The nitroethene (1.13 g, 0.005 mole) was deoxygenated in triethyl phosphite (4.98 g, 0.03 mole), over 16 h, by the general method. Chromatography on silica gave 2-phenyl-indole (0.08 g, 0.41 mmole, 8.3%), identified by its i. r. spectrum.

3) E-1-Phenyl-2-(2, 4, 6-trimethylphenyl)nitroethene. - The nitroethene (2.67 g, 0.01 mole) was deoxygenated in triethyl phosphite (6.6 g, 0.04 mole), over 18 h, by the general method. Chromatography on silica gave a bright yellow crystalline compound, identified by spectral analysis as 10a-(2, 4, 6-trimethylbenzyl)-11-(2, 4, 6-trimethylphenyl)-10aH-isoindeno[1, 2-b]quinoxaline (238), (0.02 g, 0.085 mmole, 0.85%), m. p. 215-216°. (Found: C, 86.5; H, 6.9; N, 6.0; \underline{M}^+ , 468.2577.

$C_{34}H_{32}N_2$ requires C, 87.2; H, 6.8; N, 6.0%; \underline{M} , 468.2565) δ (CDCl₃) 2.00 (6H, s), 2.07 (6H, s), 2.30 (3H, s), 2.37 (3H, s), 3.82 (2H, s), 6.87 (2H, s), 7.02 (2H, s), 7.20-7.42 (4H, m), 7.46-7.72 (2H, m), 8.40-8.62 (2H, m).



(238)

The ^{13}C n. m. r. and i. r. spectra were consistent with the assigned structure. Detailed studies of the mass spectrum (mass-analysed ion

kinetic spectrometry), performed by Professor J. H. Beynon and his co-workers at the University College of Swansea, also supported the assigned structure.

10a-(2, 4, 6-Trimethylbenzyl)-11-(2, 4, 6-trimethylphenyl)-10aH-isoindeno[1, 2-b]quinoxaline was also obtained when the reaction was carried out in t-butylbenzene (yield, 2.6%), decalin (2.1%), or benzene (5.6%). The general method was employed and 80 ml of solvent were used per 0.01 mole of the nitroethene. The reaction in t-butylbenzene or benzene also gave 1-phenyl-2-(2, 4, 6-trimethylphenyl)ethan-1-one (0.01 g, 0.042 mmole, 0.42% and 0.05 g, 0.21 mmole, 2.1%, respectively), m.p. 159-160° (lit¹⁷³ 161-162°). N.m.r. and i.r. spectra were consistent with this assignment.

4) E-1-Phenyl-2-(2, 4, 6-trimethoxyphenyl)nitroethene. - The nitroethene (3.15 g, 0.01 mole) was deoxygenated with triethyl phosphite (3.4 g, 0.02 mole) in benzene (50 ml), over 16 h, by the general method. Chromatography gave only one substance, a yellowish solid, m.p. 269-272°. The mass spectrum showed the parent ion peak to have a mass to charge ratio of 564. The yield was 0.04 g, 0.071 mmole. The i.r. spectrum showed a broad absorption at 1600 cm⁻¹ and the ¹H n.m.r. spectrum gave the following peaks; δ (CDCl₃) 3.51 (12H, s), 3.77 (6H, s), 6.07 (4H, s), 7.11-7.51 [12H(?), m]. No further data could be obtained from the small amount of material available. A tentative assignment of structure is 2, 5-diphenyl-3, 6-di-(2, 4, 6-trimethoxyphenyl)pyrazine.

5) E-2-(2, 6-Dichlorophenyl)-1-phenylnitroethene. - The nitroethene (2.94 g, 0.01 mole) was deoxygenated with triethyl phosphite (3.4 g, 0.02 mole) in benzene (50 ml), over 16 h, by the general method. Chromatography gave only one compound, a white solid, 2-(2, 6-dichlorophenyl)-N-phenylacetamide (0.08 g, 0.29 mmole, 2.9%), m.p. 222-223.5°. δ (CDCl₃) 6.77-7.70 (8H, m), 10.19 (1H, s). The i.r. spectrum showed a broad absorption at 3200 cm⁻¹ (N-H) and a strong absorption at 1655 cm⁻¹ (C=O). The mass spectrum showed parent ion peaks of mass to charge ratio 279, 281, and 283, in the pattern expected for a molecule containing two chlorine atoms. Insufficient pure material was obtained for an elemental analysis.

No products, except for triethyl phosphate (69%) could be obtained when the deoxygenation was carried out in decalin.

6) E-2-(2-Nitrophenyl)-1-phenylnitroethene. - The nitroethene (2.66 g, 0.01 mole) was deoxygenated with triethyl phosphite (3.6 g, 0.022 mole) in benzene (50 ml) over 16 h, by the general method. Small amounts of two unidentified solid substances were obtained; (i) a light brown amorphous solid (0.07 g), m. p. 201-203°; \underline{M}^+ (mass spectrum), 238. δ (DMSO- d_6) 7.20-7.65 (m), 7.80-8.32 (m). (ii) A pale yellow amorphous solid (0.08 g) m. p. 228-231°; \underline{M}^+ , 212. δ (DMSO- d_6) 6.80-7.05 (m), 7.59-7.78 (m), 8.75 (broad s).

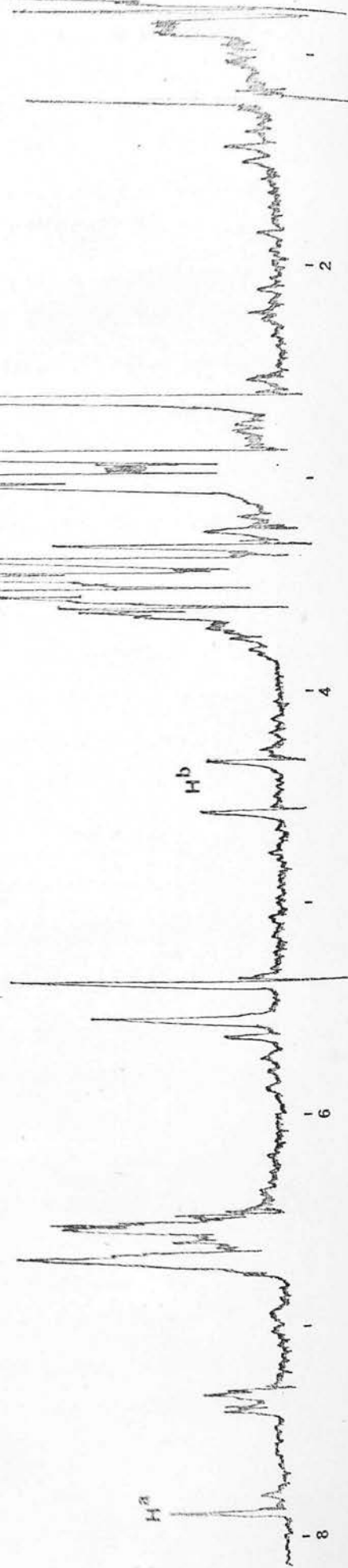
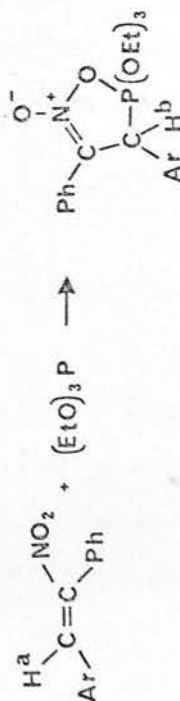
7) 1, 2, 2-Triphenylnitroethene. - The nitroethene (1.0 g, 0.003 mole) was deoxygenated with triethyl phosphite (2.0 g, 0.012 mole), over 18 h, by the general method. However, the residue obtained after the phosphite and phosphate had been removed by distillation was dissolved in a minimum of hot ethanol/water, and the solution was allowed to cool. An oil separated and slowly crystallised, at 10°. The solid was collected and recrystallised from ethanol to give 2, 3-diphenylindole (0.62 g, 0.0023 mole, 70%) m. p. 114.5-116° (lit¹⁷⁴ 122-123°), \underline{M}^+ , 269. δ (CDCl₃) 7.00-7.73 (14H, m), 8.15 (1H, broad s).

D. Observation of the Deoxygenation of 2-Aryl-1-phenylnitroethenes by ^1H and ^{31}P n. m. r. Spectroscopy.

To observe the course of a deoxygenation by n. m. r. spectroscopy, the reaction mixture, a solution of 0.25 to 0.38 mole l^{-1} of the nitroethene and 0.63 to 1.38 mole l^{-1} of the P(III) reagent in benzene- d_6 , was prepared in an n. m. r. tube. The sample was heated to 78-79° in the probe of the spectrometer, and spectra were recorded at regular intervals.

^1H n. m. r. spectra. - The course of each reaction was characterised by the gradual disappearance of the singlet peak ascribed to the olefinic hydrogen of the nitroethene (δ = 7.82-8.43). The pattern of the aromatic multiplets was observed to change and the multiplets arising

Fig.1 H-nmr Deoxygenation of 1-Phenyl-2-(2,4,6-trimethoxyphenyl)nitroethene by Triethyl Phosphite: after 28 min



from the P(III) species [$\delta = 3.62-3.92$ and $1.02-1.18$, $(\text{EtO})_3\text{P}$; $\delta = 2.80$ (d), $(\text{MeO})_3\text{P}$] became more complex as they merged with those of the increasing P(V) oxide. In addition, a doublet with a large coupling constant appeared ($\delta = 4.25-5.28$), increased in intensity to a maximum and subsequently faded during the course of the reaction. Irradiation of the phosphorus region of the spectrum (ca 40MHz) caused a collapse of the doublet to a singlet. Comparisons with authentic samples (section E) showed that 3,4-diaryl-4,5-dihydro-2-oxo-1,2,5-oxazaphosph(v)oles were most likely giving rise to these signals.

The time-scale of the reactions varied from 10 min to 6 h. Qualitatively, the rate of reaction of the nitroethenes appeared to be considerably decreased by the introduction of a di-ortho-substituted 2-aryl group, but a quantitative assessment of this effect was not attempted.

Figure 1 shows a typical spectrum recorded during the course of a reaction, when the transient doublet was at maximum intensity.

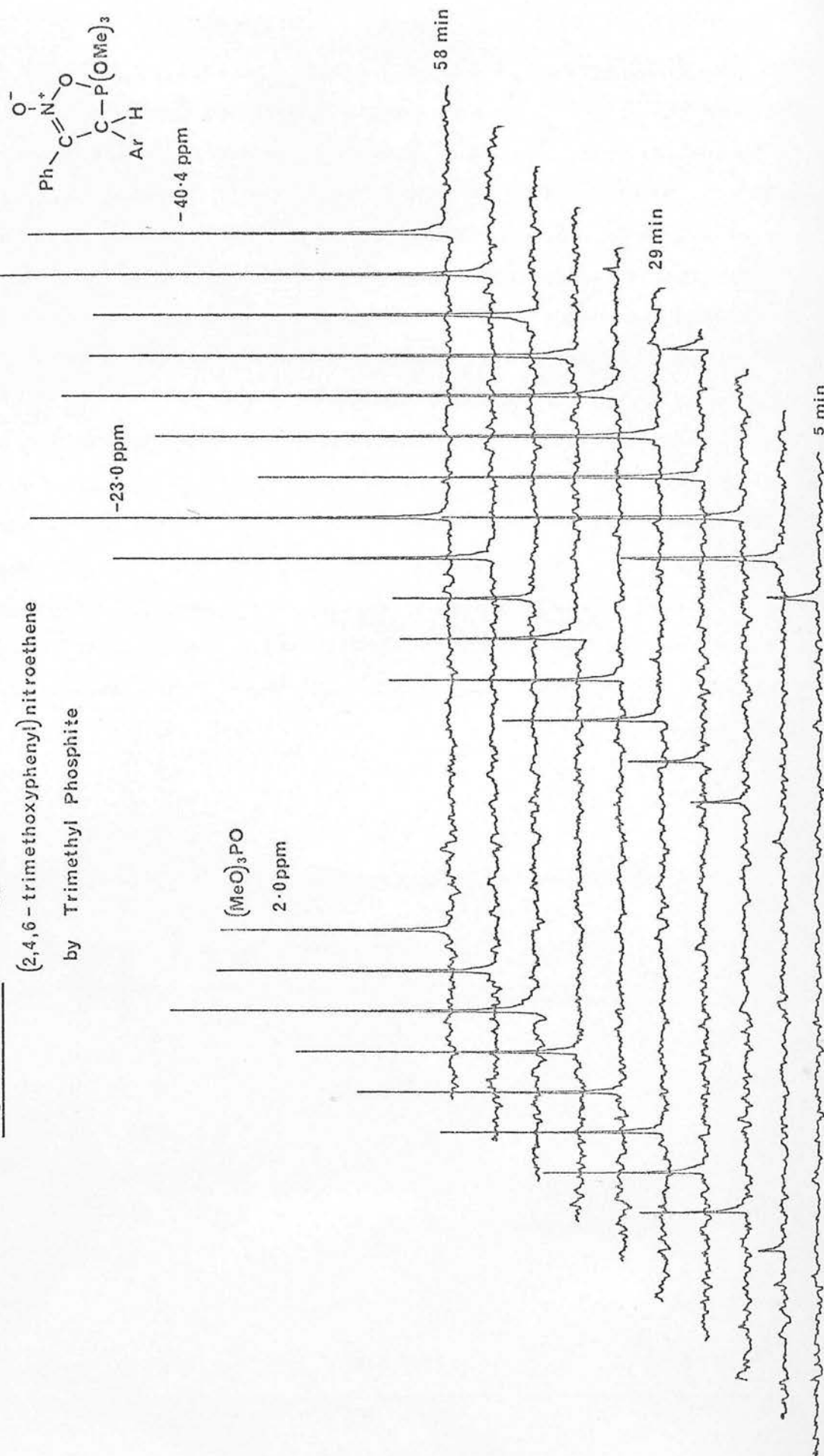
Table 3 lists the reactions which were studied and the chemical shifts and coupling constants of the transient doublets.

Table 3

¹H n. m. r. Studies of the Deoxygenation of E-2-Aryl-1-phenylnitroethenes

| Aryl group | P(III) reagent | Transient doublet (δ) | $J_{\text{P-H}}$ (Hz) |
|------------------------|--------------------------|--------------------------------|-----------------------|
| Phenyl | $(\text{MeO})_3\text{P}$ | 4.25 | 26 |
| Phenyl | $(\text{EtO})_3\text{P}$ | 4.73 | 25 |
| 2,4,6-Trimethylphenyl | $(\text{EtO})_3\text{P}$ | 4.45 ^{a)} | 28 |
| | | 5.28 | 30 |
| 2,4,6-Trimethoxyphenyl | $(\text{EtO})_3\text{P}$ | 4.45 ^{a)} | 24 |
| | | 5.20 | 28 |
| 2,6-Dichlorophenyl | $(\text{EtO})_3\text{P}$ | 5.22 | 28 |
| 2-Nitrophenyl | $(\text{EtO})_3\text{P}$ | b) | |

Fig.2 P-nmr Deoxygenation of 1-Phenyl-2-(2,4,6-trimethoxyphenyl)nitroethene by Trimethyl Phosphite



- a) Two transient doublets were observed in this case.
 b) No transient doublet was observed in this case.

The deoxygenation of β -nitrostyrene (2-phenylnitroethene) by trimethyl phosphite was also studied by ^1H n. m. r. spectroscopy. The spectra showed the same general trend as for the α -nitrostilbenes described above, except that instead of a transient doublet, a complex pattern of peaks appeared ($\delta = 5.12$ - 5.90) and gradually resolved into 4 doublets of equal intensity at $\delta = 5.12$, 5.58 , 5.65 , and 5.87 ($J = \text{ca. } 2\text{Hz}$ in each case). The structural origin of these signals was undetermined.

^{31}P n. m. r. spectra. - For each reaction ten spectra were recorded automatically at regular intervals and displayed on one chart to provide a record open to rapid visual interpretation. Figure 2 shows a typical set of spectra. Each reaction was characterised by the steady increase in intensity of a peak corresponding to the oxidised P(III) reagent. A peak with a chemical shift in the range $\delta = -15.55$ to -42.32 (indicative of a pentaco-ordinate phosphorane species) was also observed to grow in intensity, to reach a steady-state maximum before diminishing again as the reaction proceeded. Comparisons with authentic samples (section E) showed that these phosphoranes were 3,4-diaryl-4,5-dihydro-2-oxo-1,2,5-oxazaphosph(v)oles.

In several reactions a similar behaviour was observed of a peak in the range $\delta = -4.44$ to -27.77 . This peak appeared later in the course of the reaction and generally did not reach as great an intensity as the earlier transient peak. A group of peaks in the range $\delta = 12$ - 31 , most likely resulting from various phosphonate or phosphinate esters, grew steadily throughout the course of those reactions which involved unsubstituted α -nitrostilbene.

The reactions were observed for between 26 and 84 minutes, and the rates of reaction were found qualitatively to depend on the substituents of the 2-aryl groups of the nitroethene and on the tervalent phosphorus reagents. The order of the rates of reaction was phenyl > 2-nitrophenyl > 2,6-dichlorophenyl > 2,4,6-trimethylphenyl \approx 2,4,6-trimethoxyphenyl, and $(\text{EtO})_3\text{P} \approx \text{PhP}(\text{OMe})_2 \approx \text{PhPOCH}_2\text{CH}_2\text{O} > (\text{MeO})_3\text{P}$.

It was noted that occasionally the intensity of a peak in a set of spectra did not correspond to the overall pattern of the reaction. "False" results of this type are a result of the digital sampling technique of the spectrometer. To keep such results to a minimum, the observation "window" was generally set at +40 to -60 p. p. m., which meant that the signal due to the P(III) reagent ($\delta \gg 40$) was not observed.

Table 4 lists the reactions which were studied, and the chemical shifts of the transient phosph(v)oles and of the oxidised P(III) reagents.

Table 4

^{31}P n. m. r. Studies of the Deoxygenation of E-2-Aryl-1-phenylnitroethenes

| Aryl group | P(III) reagent | Oxide (δ) | Phosph(v)ole (δ) |
|-----------------------------|---|--------------------|---|
| Phenyl | $(\text{MeO})_3\text{P}$ | 1.88 | -38.14 -25.41 ^{a)} |
| Phenyl | $(\text{EtO})_3\text{P}$ | -1.60 | -40.24 -27.77 ^{a)} |
| Phenyl | $(\text{MeO})_2\text{PPh}$ | 7.89 | -15.55 |
| Phenyl ^{b)} | $\text{PhP} \overline{\text{OCH}_2\text{CH}_2\text{O}}$ | 34.71 | -17.90 ^{c)} -18.35 |
| 2,4,6-Trimethylphenyl | $(\text{MeO})_3\text{P}$ | 2.02 | -40.20 -23.93 ^{a)} |
| 2,4,6-Trimethylphenyl | $(\text{EtO})_3\text{P}$ | -1.18 | -42.32 -26.34 ^{a)} |
| 2,4,6-Trimethylphenyl | $\text{PhP} \overline{\text{OCH}_2\text{CH}_2\text{O}}$ | 35.80 | -20.57 ^{d)} -21.01 -4.44 ^{a)} |
| 2,4,6-Trimethoxyphenyl | $(\text{MeO})_3\text{P}$ | 2.03 | -40.37 -23.02 ^{a)} |
| 2,4,6-Trimethoxy- phenyl | $\text{PhP} \overline{\text{OCH}_2\text{CH}_2\text{O}}$ | 33.70 | -20.94 ^{e)} -21.89 -5.06 ^{a)} |

Table 4 (cont.)

| Aryl group | P(III) reagent | Oxide (δ) | Phosph(v)ole (δ) |
|---------------------|---|--------------------|--|
| 2, 6-Dichlorophenyl | (MeO) ₃ P | 1.92 | -25.09 |
| 2, 6-Dichlorophenyl | (EtO) ₃ P | -1.24 | -35.55 -27.63 ^{a)} |
| 2, 6-Dichlorophenyl | PhP $\overline{\text{POCH}_2\text{CH}_2\text{O}}$ | 33.68 | -23.68 ^{f)} -25.05 - 6.90 ^{a)} |
| 2-Nitrophenyl | (MeO) ₃ P | 1.84 | -25.32 |
| 2-Nitrophenyl | PhP $\overline{\text{POCH}_2\text{CH}_2\text{O}}$ | 33.84 | -19.77 ^{g)} -20.66 -5.15 ^{a)} -0.64 ^{a)} |

- a) A phosph(v)ole structure for these compounds was not confirmed.
- b) Reaction temperature = 50°.
- c) The two peaks correspond to two possible diastereoisomers of the phosph(v)ole. The initial intensity ratio was 2:1 (respectively).
- d) As c). The initial intensity ratio was 1.4:1 (resp). This ratio changed steadily throughout the reaction, and after 54 min was 1:1.9.
- e) As c). The initial intensity ratio was 1.3:1 (resp). This ratio changed steadily throughout the reaction and after 84 min was 1:3.7.
- f) As c). The initial intensity ratio was 1.4:1 (resp) but after 29 min only the latter peak could be observed.
- g) As c). The initial intensity ratio was 3.5:1 (resp) but after 25 min only the former peak could be observed.

The deoxygenation of 1, 2, 2-triphenylnitroethene by trimethyl phosphite was also observed by ^{31}P n. m. r. A peak corresponding to trimethyl phosphate ($\delta = 1.99$) grew steadily, but at a rate which was much slower than in the reactions listed above. No peak corresponding to a phosphorane was observed.

During the deoxygenation of β -nitrostyrene by trimethyl phosphite, a peak corresponding to $(\text{MeO})_3\text{PO}$ grew rapidly and reached a steady maximum intensity after ca 15 min. A cluster of peaks which appeared in the range $\delta = 16.11$ to 18.91 showed the same behaviour. A peak possibly corresponding to a pentaco-ordinate phosph(v)ole made a transient appearance at $\delta = -27.67$. The intensity of this peak, which was considerably lower than the intensities of corresponding peaks in the above reactions, reached a maximum after ca 9 min.

E. 1, 2, 5-Oxazaphosph(v)ole-2-oxides

1) Preparation and Structure

Tables 5 and 6 list the 1, 2, 5-oxazaphosph(v)ole-2-oxides, all new compounds, which were prepared by the reaction of a tervalent phosphorus reagent with a 1, 2-diarylnitroethene in t-butanol at room temperature.

Details of the experimental procedure follow the tables.

Table 5

3,4-Diaryl-4, 5-dihydro-5, 5, 5-trialkoxy-1, 2, 5-oxazaphosph(v)ole-2-oxides



| Compound | R ¹ | R ² | R ³ | R ⁴ | Yield ^{a)} % | M. p. °C | Analysis (%) ^{b)} | | |
|----------|----------------|-----------------|----------------|----------------|--------------------------|-------------|----------------------------|-----|-----|
| | | | | | | | C | H | N |
| A | Me | H | H | H | 85 | 113.5-114.5 | 58.3 | 5.8 | 4.0 |
| | | | | | | | 58.5 | 5.7 | 4.0 |
| B | Me | Cl | Cl | H | 27 | 119.5-120 | 48.6 | 4.3 | 3.4 |
| | | | | | | | 48.8 | 4.3 | 3.4 |
| C | Me | Me | Me | Me | 37 | 107-108.5 | 61.2 | 6.6 | 3.7 |
| | | | | | | | 61.4 | 6.7 | 3.6 |
| D | Me | OMe | OMe | OMe | 73 | 116-118 | 54.6 | 5.7 | 3.3 |
| | | | | | | | 54.7 | 5.9 | 3.2 |
| E | Me | NO ₂ | H | H | 82 | 115.5 dec | 51.8 | 4.8 | 7.0 |
| | | | | | | | 51.8 | 4.8 | 7.1 |
| F | Et | H | H | H | 48 | 63-65 | c) | | |
| G | Et | Me | Me | Me | 34 | 80-83 | 63.2 | 7.4 | 3.2 |
| | | | | | | | 63.1 | 7.4 | 3.2 |

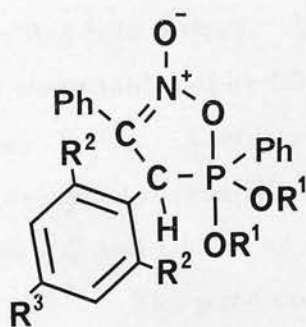
a) Yields based on starting 1, 2-diarylnitroethenes.

b) Upper row, "Found" values; Lower row, "Required" values.

c) A satisfactory analysis was not obtained.

Table 6

5, 5-Dialkoxy-4, 5-dihydro-3, 4, 5-triaryl-1, 2, 5-oxazaphosph(v)ole-2-oxides



| Compound | R ¹ | R ² | R ³ | Yield ^{a)} | | Analysis (%) ^{b)} | | |
|----------|------------------------------------|----------------|----------------|---------------------|------------|----------------------------|-----|-----|
| | | | | % | M. p. (°C) | C | H | N |
| H | Me | H | H | 83 | 119 dec | 66.6 | 5.6 | 3.5 |
| | | | | | | 66.8 | 5.6 | 3.5 |
| I | Me | Cl | H | 92 | 88.5 dec | 56.9 | 4.4 | 3.0 |
| | | | | | | 56.9 | 4.3 | 3.0 |
| J | Me | Me | Me | 54 | 106 dec | 68.5 | 6.4 | 3.2 |
| | | | | | | 68.7 | 6.4 | 3.2 |
| K | Me | OMe | OMe | 81 | 102 dec | 61.8 | 5.8 | 2.8 |
| | | | | | | 61.9 | 5.8 | 2.9 |
| L | -(CH ₂) ₂ - | H | H | 83 | 137-141 | 66.9 | 5.2 | 3.3 |
| | | | | | | 67.2 | 5.1 | 3.6 |
| M | -(CH ₂) ₂ - | Cl | H | 81 | 118 dec | 57.0 | 4.0 | 2.9 |
| | | | | | | 57.1 | 3.9 | 3.0 |
| N | -(CH ₂) ₂ - | OMe | OMe | 77 | 122-124 | 61.9 | 5.5 | 2.9 |
| | | | | | | 62.1 | 5.4 | 2.9 |

a) Yields based on starting 1, 2-diarylnitroethenes.

b) Upper row, "Found" values; Lower row, "Required" values.

The phosphorus(III) reagent (0.025 mole, or 0.01 mole in the case of $\text{Ph}\overline{\text{POCH}_2\text{CH}_2\text{O}}$) was dissolved in t-butanol (25 ml) and the 1, 2-diarylnitroethene (0.01 mole) was added. The mixture was stirred at room temperature until all the nitroethene was consumed (t.l.c.).

Reaction times varied from 0.5 h to 3 days. Compounds A to E, H, I, K, M, and N precipitated and were isolated by filtration, washed with ether, and dried under vacuum over P_2O_5 . Compounds F, G, J, and L required removal of solvent and excess phosphorus(III) reagent under vacuum before they were obtained as solids (G and L), or as oils (F and J) which crystallised on standing at -20° . The pure compounds could be stored indefinitely at -20° .

The structure of the 1, 2, 5-oxazaphosph(v)oles was confirmed by

n. m. r. and i. r. data. In particular, the compounds all exhibited negative ^{31}P chemical shifts and examination of the ^1H n. m. r. spectrum of the parent compound (A) at -60° showed three separate methoxy signals (instead of one equivalent methoxy signal observed at room temperature) which is indicative of a restriction of pseudorotation about the pentacoordinate phosphorus atom. Other details of the spectra which support the assigned structure are listed in Tables 7 and 8.

Table 7

^{31}P and ^1H n. m. r. data for 3,4-diaryl-4,5-dihydro-5,5,5-trialkoxy-1,2,5-oxazaphosph(v)ole-2-oxide

| | Compound ^{a)} | | | | | | |
|----------------------------------|------------------------|-----------------------|--|---|-----------------------|-----------------------|-----------------------|
| | A | B | C | D | E | F | G |
| ^{31}P (δ) | | | | | | | |
| CDCl_3 | -36.6 | -42.7 | -38.6 | -39.1 | -39.3 | -37.6 | -40.5 |
| C_6D_6 | -38.9 | b) | -40.2 | -40.4 | b) | -40.0 | b) |
| ^1H (CDCl_3) | | | | | | | |
| δ -Ar | 7.96(m) 7.32(m) | 7.78(m) 7.12(m) | 7.82(m) 7.21(m) | 7.90(m) 7.14(m) | 8.21(m) 7.87(m) | 7.93(m) 7.28(m) | 7.82(m) 7.16(m) |
| | | | 6.76(d) ^{c)} | 6.00(s) broad ^{c)} | 7.40(m) | | 6.74(d) ^{f)} |
| δ -(Ar) OCH_3 | - | - | - | 3.78(s) broad ^{c)} 3.65(s) | - | - | - |
| δ -(Ar) CH_3 | - | - | 2.52(d) ^{c, d)} 2.26(d) ^{c, d)} 2.19(d) ^{c, d)} | | | | |
| δ -CH | 4.68(d) ^{e)} | 5.78(d) ^{f)} | 5.14(d) ^{g)} | 5.40(d) ^{h)} | 5.84(d) ^{e)} | 4.70(d) ^{j)} | 5.13(d) ^{g)} |
| δ - OCH_3 | 3.64(d) ^{j)} | 3.66(d) ^{k)} | 3.67(d) ^{j)} | 3.61(d) ^{j)} | 3.61(d) ^{j)} | - | - |
| δ - OCH_2 | - | - | - | - | - | 3.99(m) | 4.03(m) |
| δ -C- CH_3 | - | - | - | - | - | 1.10(m) | 1.16(m) |

- a) Compounds numbered as in Table 5. b) Not recorded.
- c) The meta-H's of the substituted 4-aryl group and the H's of the ortho-substituents are non-equivalent, indicating that rotation of the 4-aryl group is restricted.
- d) $J_{P-H} = 2\text{Hz}$. e) $J_{P-H} = 26\text{Hz}$. f) $J_{P-H} = 29\text{Hz}$.
- g) $J_{P-H} = 30\text{ Hz}$. h) $J_{P-H} = 27.5\text{Hz}$. i) $J_{P-H} = 25\text{Hz}$.
- j) $J_{P-H} = 12.5\text{Hz}$. k) $J_{P-H} = 13\text{Hz}$.

Table 8

^{31}P and ^1H n.m.r. data for 5,5-dialkoxy-4,5-dihydro-3,4,5-triaryl-
1,2,5-oxazaphosph(v)ole-2-oxides

Compound^{a)}

H I J K L M N

^{31}P (δ)

| | | | | | | | |
|-------------------|----|---------------------|---------------------|------------------------|---------------------|---------------------|---------------------|
| CDCl ₃ | b) | -33.6 | -24.5 | -26.6 | -16.0 ^{e)} | -21.5 ^{f)} | -18.4 ^{g)} |
| | | broad ^{c)} | broad ^{c)} | broad ^{c, d)} | 16.9 | -23.2 | -19.8 |
| | | | | -29.4 | | | |
| | | | | broad ^{c, d)} | | | |

^1H (CDCl₃)

| | | | | | | | |
|--------------------------------|----|------------------|--|----------------------|------------------|------------------|---|
| δ -Ar | b) | 6.90- 8.10(m) | 7.00- 8.00(m) | 7.00- 8.10(m) | 7.00- 8.30(m) | 6.80- 8.30(m) | 7.00- 8.20(m) |
| | | | 6.58(s) ^{h)} | 6.10 | | | 6.00- |
| | | | 6.92(s) ^{h)} | broad ^{h)} | | | 6.22(m) |
| δ -(Ar)OCH ₃ | - | - | - | ca 3.7 ⁱ⁾ | - | - | 2.78(s) 3.70(s) ^{h)} 3.75(s) ^{h)} |
| δ -(Ar)CH ₃ | - | - | 2.62(s) ^{j)} 2.19(d) ^{k, h)} 1.93 broad ^{c, h, l)} | - | - | - | - |

| | H | I | J | K | L | M | N |
|--|----|--|--|--------------------------------|--|--|--|
| δ -CH | b) | 6.10(d) ^{m)} | 5.38(d) ⁿ⁾ | 5.70(d) ^{o)} | 4.96(d) ^{e, p)} 4.74(d) ^{e, q)} | 6.15(d) ^{e, r)} 6.01(d) ^{e, s)} | 5.68(d) ^{e)} 5.56(d) ^{e)} |
| δ -OCH ₃ | b) | 3.93(s) broad ^{v)} 3.13(s) broad ^{v)} | 4.08(d) broad ^{v, w)} 2.95(d) broad ^{v, x)} | 2.80- 4.30(m) ⁱ⁾ | - | - | - |
| δ -(OCH ₂) ₂ | - | - | - | - | 3.22- 4.14(m) | 3.40- 4.30(m) | 3.28- 4.10(r) |

- a) Compounds numbered as in Table 6. b) A solvent for this compound could not be found. c) Line broadening is caused by interchange of diastereoisomers via pseudorotation: probe temperature, 25°C. d) Pseudorotation is sufficiently slow in this case to permit partial resolution of the signals of the two diastereoisomers. e) Pseudorotation leading to interchange of diastereoisomers is hindered by the spirobicyclic structure, resulting in complete resolution of the two n.m.r. signals. The intensity ratio is 1:2, respectively. f) As e), but the intensity ratio is 2.5:1, respectively. g) As e) but the intensity ratio is 1.4:1, respectively. h) The observation of broad or resolved signals for the meta-H's and H's of the ortho-substituents of the 4-aryl group indicates that rotation of the group is restricted. i) Exact positions of the signals are concealed by line broadening and superposition of a second set of methoxy signals. j) $J_{P-H} = 1\text{Hz}$. k) $J_{P-H} = 2\text{Hz}$. l) One ortho-methyl group is particularly affected by the nature of the diastereoisomers. m) $J_{P-H} = 22\text{Hz}$. n) $J_{P-H} = 28\text{Hz}$. o) $J_{P-H} = 24\text{Hz}$. p) $J_{P-H} = 26\text{Hz}$. q) $J_{P-H} = 16\text{Hz}$. r) $J_{P-H} = 32.5\text{Hz}$. s) $J_{P-H} = 18\text{Hz}$. t) $J_{P-H} = 29\text{Hz}$. u) $J_{P-H} = 19\text{Hz}$. v) Line broadening is caused by interchange of apical and equatorial methoxy-groups via pseudorotation: probe temperature, 28°C. w) $J_{P-H} = 13\text{Hz}$. x) $J_{P-H} = 9\text{Hz}$.

The i. r. spectra of the 1, 2, 5-oxazaphosph(v)oles were as expected. For example, in the case of compound (A) there was no signal

ascribable to (P=O), but a multiple line with peaks at 1040, 1070, and 1095 cm^{-1} was ascribed to the P-O-C grouping.¹¹¹

2) Deoxygenation and thermal decomposition of 1, 2, 5-oxaza-phosph(v)ole-2-oxides

a) 4, 5-Dihydro-3, 4-diphenyl-5, 5, 5-trimethoxy-1, 2, 5-oxaza-phosph(v)ole-2-oxide.

i) Reaction with trimethyl phosphite. - After the phosph(v)ole (1.75 g, 0.005 mole) had been heated with trimethyl phosphite (2.23 g, 0.018 mole) for 16 h, under N_2 , unreacted $(\text{MeO})_3\text{P}$ and trimethyl phosphate (1.03 g, 0.007 mole) were removed by Kugelrohr distillation. The residue was dissolved in hot ethanol/water. When the solution cooled, 0.14 g of a solid was obtained. Examination of the solid by t.l.c. showed that it was a complex mixture, one component of which had an R_f value similar to that of authentic 2-phenylindole. However, chromatography on silica failed to give any identifiable products. Similar results were obtained when the reaction was carried out in benzene or t-butylbenzene. In one case only, when an old sample of phosph(v)ole, which, by n.m.r., had slightly decomposed, was allowed to react with $(\text{MeO})_3\text{P}$ in benzene for 3 h at the boiling point, work-up and chromatography on silica gave an impure sample of 2-phenylindole (0.05 g, 0.26 mmole, 10%), identified by its i.r. spectrum.

ii) Reaction with PCl_3 . - Freshly distilled PCl_3 (0.69 g, 0.005 mole) was added to a solution of the phosph(v)ole in dry chloroform or benzene. The solution became greeny-blue in colour and a noticeable warming occurred within one minute. T.l.c. examination showed several spots which were unchanged after the solutions had been boiled and re-tested. However work-up and chromatography failed to give any identifiable compounds. When the reaction was carried out in the ^{31}P n.m.r. probe at -70° and $+70^\circ$, several unidentified peaks were observed in the range -10 to +20 p.p.m.

iii) Thermal decomposition. - A solution of the phosph(v)ole

(3.49 g, 0.01 mole) in dry benzene (25 ml) was boiled under N_2 for 16 h. Kugelrohr distillation gave trimethyl phosphate (0.51 g, 3.6 mmole, 36%). An attempt to crystallise the residue from hot methanol/water gave only tar. T.l.c. examination showed several components, one of which had a similar R_f to authentic 2-phenylindole, but preparative chromatography failed to give any identifiable compounds.

A sample of the phosph(v)ole (6.4 g) was allowed to stand in a sealed glass jar at room temperature for 14 days. The compound decomposed to a viscous brown oil which, on chromatography, gave pale yellow crystals of dimethyl(1, 2-diphenyl)ethan-1-one-2-phosphonate (0.69 g, 2.27 mmole, 12.4%), m.p. 134-136°. (Found: C, 62.9; H, 5.6. $C_{16}H_{17}O_4P$ requires C, 63.2; H, 5.55%). ^{31}P n.m.r., $\delta = 22.5$; 1H n.m.r. $\delta = 7.85-8.03$ (m, 2H), 7.10-7.60 (m, 8H), 5.34 (d, 1H), 3.75 (d, 3H), and 3.65 (d, 3H).

b) 4, 5-Dihydro-3, 4-diphenyl-5, 5, 5-triethoxy-1, 2, 5-oxaza-phosph(v)ole-2-oxide.

Reaction with triethyl phosphite. (i) The phosph(v)ole (1.98 g, 0.005 mole) was added to triethyl phosphite (1.99 g, 0.012 mole) and the mixture was boiled under reflux, under N_2 , for 16 h. Examination by h.p.l.c. suggested that 2-phenylindole might be present in small amount, but preparative chromatography afforded no identifiable products.

(ii) The reaction was carried out as in (i), but with 25 ml benzene or 15 ml decalin as solvent. In both cases no products could be identified or isolated.

c) 4, 5-Dihydro-3-phenyl-4-(2, 4, 6-trimethylphenyl)-5, 5, 5-triethoxy-1, 2, 5-oxazaphosph(v)ole-2-oxide.

(i) Reaction with triethyl phosphite. - The phosph(v)ole (1.0 g, 0.0023 mole) was heated with triethyl phosphite (2 g, 0.012 mole) at the boiling point for 16 h under N_2 , then excess phosphite was removed by distillation. T.l.c. examination of the residue showed three spots, one of which exhibited a bright yellow fluorescence and an R_f value similar to that of 10a-(2, 4, 6-trimethylbenzyl)-11-(2, 4, 6-trimethylphenyl)-10aH-

isoindeno[1, 2-b]quinoxaline (see section C. 3). However chromatography on silica gave only an oil (0.26 g) which consisted of several components (t.l.c.), including the suspected quinoxaline. Further attempts at separation and purification were unsuccessful.

(ii) Thermal decomposition. - The phosph(v)ole (0.35 g, 0.81 mmole) was dissolved in dry benzene (10 ml) and the solution boiled, under N_2 , for 14 h. T.l.c. examination showed at least ten poorly resolved components, and separation was not attempted.

d) 4, 5-Dihydro-3-phenyl-4-(2, 4, 6-trimethylphenyl)-5, 5, 5-trimethoxy-1, 2, 5-oxazaphosph(v)ole-2-oxide.

(i) Reaction with trimethyl phosphite. - The phosph(v)ole (1 g, 0.0026 mole) was heated with trimethyl phosphite (2 g, 0.016 mole). Once the excess phosphite had been removed by distillation, chromatography of the residue gave only a yellow oil which was shown to consist of several unidentified components by t.l.c. and n.m.r. examination.

(ii) Thermal decomposition. - The phosph(v)ole (1 g, 0.0026 mole) was dissolved in dry decalin (10 ml) and the solution was boiled, under N_2 , for 18 h. T.l.c. examination showed several decomposition products, none of which could be identified.

e) Attempted cycloaddition reactions. - 4, 5-Dihydro-3, 4-diphenyl-5, 5, 5-trimethoxy-1, 2, 5-oxazaphosph(v)ole-2-oxide (0.35 g, 0.001 mole) was dissolved in dichloromethane (10 ml) together with either methyl methacrylate (0.17 g, 0.002 mole) or cyclohexene (0.16 g, 0.002 mole). After the solutions had stood at room temperature for 84 h the volatile components were removed under vacuum to leave a caked white solid. I.r. examination showed that this was slightly impure phosph(v)ole, in both cases, and no evidence for cycloaddition could be found.

3) Observation by ^{31}P and 1H n.m.r. of some reactions of 4, 5-dihydro-3, 4-diphenyl-5, 5, 5-trimethoxy-1, 2, 5-oxazaphosph(v)ole-2-oxide.

a) Reaction with trimethyl phosphite.

(i) 1H n.m.r. - A solution of the oxazaphosph(v)ole (0.2 mmole)

and trimethyl phosphite (0.8 mmole) in C_6D_6 (0.5 ml) was prepared in an n.m.r. tube, and the spectrum was recorded. The sample was heated at 78° in the probe of the spectrometer and spectra were recorded at regular intervals. After 30 min the original doublet at $\delta = 4.26$ was reduced to ca half of its original intensity relative to the aromatic peaks. An aromatic multiplet at $\delta = 7.20-7.34$ also appeared during this time. After ca 8 h the doublet ($\delta = 4.26$) and all aromatic peaks except a group at $6.40-6.90$ had disappeared.

(ii) ^{31}P n.m.r. - A solution was prepared as in (i), except that the amount of $(MeO)_3P$ used was 0.4 mmol. The sample was heated to 78° in the probe of the spectrometer and 10 spectra were recorded at 12.5 min intervals. The following observations were made: a peak at $\delta = -38.34$, corresponding to the starting phosph(v)ole slowly decreased in intensity; a peak at $\delta = -25.45$ increased in intensity, reached a maximum after 60-70 min and then started to decrease; a peak at $\delta = 1.98$, corresponding to $(MeO)_3PO$, increased steadily throughout the reaction; a minor peak at $\delta = 21.33$ increased steadily throughout the reaction.

b) Thermal decomposition

(i) 1H n.m.r. - An n.m.r. sample consisting of the oxazaphosph(v)ole (ca 0.2 mmol) in C_6D_6 (0.5 ml) was heated at 75° in the n.m.r. probe. The spectra recorded at regular intervals showed the steady disappearance of the starting material, and the growth of a complex array of product signals.

(ii) ^{31}P n.m.r. - A sample, as in (i), was heated in the ^{31}P n.m.r. probe at 79° and ten spectra were recorded at regular 5 min intervals. The single peak of the starting material ($\delta = -38.9$) steadily decreased in intensity and had disappeared after 30 min. At the same time a peak corresponding to $(MeO)_3PO$ ($\delta = 1.9$) grew steadily. No other peaks were observed.

c) Miscellaneous

(i) Attempted ligand exchange. - To a solution of 4,5-dihydro-3,4-diphenyl-5,5,5-trimethoxy-1,2,5-oxazaphosph(v)ole-2-oxide in C_6D_6 in an n.m.r. tube was added a few drops of dry ethylene glycol. The solution was shaken thoroughly and left at room temperature for 3 days.

Examination by ^{31}P n.m.r. showed that none of the original phosph(v)ole remained, but neither was there evidence for a phosph(v)ole formed by ligand exchange. Many peaks were observed between -1.3 and 41.4 p.p.m.

(ii) The oxazaphosph(v)ole (0.2 mmole) and dimethylphenylphosphonite (0.4 mmole) were dissolved in C_6D_6 (0.5 ml) and the ^{31}P n.m.r. spectrum was recorded. Further spectra were recorded after the sample had stood for 7 h and 16 h at room temperature and after 6 min at 50° . There was no indication of any reaction other than slight decomposition of the oxazaphosph(v)ole.

(iii) The ^1H n.m.r. spectrum of the spirophosphorane (L; Table 6; section E.1) was recorded and showed clearly the presence of two diastereoisomers. As the temperature of the sample was raised to 65° the signals of one diastereoisomer increased at the expense of the other. When the solution was cooled no reversion to two forms occurred. The ^{31}P n.m.r. spectrum of the final solution confirmed the presence of only one isomer.

F. Thermal Decomposition of Aryl 2-Azidophenyl Ethers and Sulphides and Deoxygenation of Aryl 2-Nitrophenyl Ethers.

1) General method. - The solvent, decalin or triethyl phosphate (15-50 ml), was purged of oxygen by bubbling dry N_2 through it for 15 min and was heated to $160\text{-}165^\circ$. The azide (0.1-10 mmole) was added in portions over 15-30 min, with stirring, then the temperature was raised to ca 200° for 1 to 2 h. The solutions were subsequently examined by h.p.l.c. In addition those samples involving the larger amounts of azide were worked up by distilling off the solvent and separating compounds of the residue by column chromatography.

H.p.l.c. was used quantitatively when appropriate. 1-Chloro-2,4-dinitrobenzene was used as an internal standard, and relative detector responses to authentic samples of products were determined by examination of known mixtures.

a) 2-Azidophenyl 2',6'-dimethylphenyl ether. - Decomposition of

the azide (2.45 g, 0.01 mole) in $(\text{EtO})_3\text{PO}$ (50 ml) led to the isolation of 5,11-dihydro-4-methyldibenz[b, e][1,4]oxazepine (1.0 g, 4.8 mmole, 48%), m. p. 120-122° (lit^{58a} 120-121°, mixed m. p. 119-122°) which was identical to an authentic sample.

b) 2-Azidophenyl 2',4',6'-trimethylphenyl ether. - After decomposition of the azide (0.70 g, 2.8 mmole) in $(\text{EtO})_3\text{PO}$ (25 ml), an h. p. l. c. study of the reaction mixture showed that 5,11-dihydro-2,4-dimethyldibenz[b, e][1,4]oxazepine (identified by comparisons of retention times on h. p. l. c. and R_f values on t. l. c.) had been formed in good yield (51%).

c) 2-Azidophenyl 2',6'-dimethoxyphenyl ether. - Decomposition of the azide (1.1 g, 4.1 mmole) in $(\text{EtO})_3\text{PO}$ led to the isolation of 4-methoxyphenoxazine (0.14 g, 0.66 mmole, 16%), m. p. 79-80° (lit^{58a} 81-82°), and 1,2-dimethoxyphenoxazine (0.011 g, 4.5×10^{-5} mole, 1.1%) which failed to crystallise. Both compounds were identified by comparison of i. r. and n. m. r. data with authentic samples.^{58a}

d) 2-Azidophenyl 2',6'-dichlorophenyl ether. - The azide (1.02 g, 3.66 mmole) was decomposed in $(\text{EtO})_3\text{PO}$ (25 ml), but no products could be isolated from the reaction mixture. H. p. l. c. and t. l. c. examination showed that there were many components in the mixture. A similar result was obtained when the decomposition was carried out in decalin.

e) 2-Azidophenyl 4'-chlorophenyl ether. The azide (2.2 g, 8.8 mmole) was decomposed in $(\text{EtO})_3\text{PO}$ (25 ml). H. p. l. c. and t. l. c. examination of the reaction mixture showed several poorly resolved components, one of which was predominant. However, chromatography failed to provide any identifiable components.

f) 2-Azidophenyl 2',6'-dichlorophenyl sulphide. - Authentic samples of the known decomposition products of the azide, 1-chlorophenothiazine (0.0157 g, 0.069 mmole) and 4-chlorophenothiazine (0.0119 g, 0.052 mmole) were dissolved in decalin (15 ml). The general procedure was then followed for the addition of the azide (0.0583 g, 0.197 mmole). The solution was heated to reflux for 2 h after addition of the azide, after which the amounts of 1-chlorophenothiazine (0.0089 g, 0.039 mmole) and 4-chlorophenothiazine (0.0046 g, 0.020 mmole) in the reaction mixture were determined

by h. p. l. c.

g) Stability of 5, 11-Dihydro-4-methyldibenz[b, e][1, 4]oxazepine . -

The oxazepine (0.1 g, 0.47 mmole) was dissolved in $(\text{EtO})_3\text{PO}$ or decalin (15 ml), and a small sample of the solution retained. The bulk was then purged of oxygen with N_2 and heated at ca 200° for 2 h. A further sample was then taken and compared with the initial sample by h. p. l. c. No evidence of decomposition of the product was observed in the decalin case, and only a trace of decomposition was observed in the $(\text{EtO})_3\text{PO}$ case.

2) Deoxygenation of 2', 6'-dimethyl- and 2', 4', 6'-trimethylphenyl 2-nitrophenyl ethers.

General method. - Small scale reactions only were carried out, and examination of the final reaction mixtures was by h. p. l. c. The solution of nitro-compound (0.5 mmole) and $(\text{EtO})_3\text{P}$ (3 mmole) in $(\text{EtO})_3\text{PO}$ (4 ml) was purged of oxygen by N_2 and heated at 152° for 65 h. Examination of the reaction mixtures by h. p. l. c. showed that the major single peak resulted from the superposition of the expected oxazepine (as in 1. a and 1. b above) and starting material peaks. Conditions for satisfactory resolution of these peaks could not be found.

G. Deoxygenation of Nitroxyl Radicals by Triethyl Phosphite.

General method. - The nitroxyl radical was freshly prepared from the corresponding hydroxylamine (section B. 5) and was accurately weighed (0.840 mmole to 1.600 mmole). It was then dissolved in the dry alcohol (25 ml), and triethyl phosphite (0.50 ml, 2.9 mmole) was added by pipette. Dry lithium chloride (5 g, 0.1 mole) was added, when required, and the solution was then purged of dissolved oxygen by passing a stream of dry nitrogen through it for 10-15 min. The solution was boiled under reflux, under nitrogen, and with stirring, for 64 h. The solvent was then removed by evaporation in vacuo and the residue was extracted with ether (25 ml). The ether solution was shaken with dilute hydrochloric acid

(2 x 20 ml) and the combined aqueous extracts were subsequently basified by addition of dilute sodium hydroxide solution. The final aqueous solution was extracted with ether (2 x 20 ml) and an accurately weighed sample of bibenzyl was dissolved in the combined ether solutions. The solution was evaporated to a few ml and samples of this final solution were examined by g.l.c. The components of the mixture were first identified by g.l.c. /m. s. and subsequently by comparison of retention times with authentic samples. The yields of products were calculated by measuring the areas of the peaks relative to bibenzyl (manually or by electronic integration), taking into due consideration the variation in sensitivity of the flame ionisation detector to different compounds. The correction factors were determined by preparing samples containing known amounts of authentic products and bibenzyl and examining these by g.l.c. Measurement of peak area ratios and comparison with the known molar ratios permitted calculation of the required correction factors.

Table 9 lists the experiments which were carried out and the products and yields which were obtained.

Table 9

Deoxygenation of Nitroxyl Radicals

| Nitroxyl | Solvent | LiCl ^{c)} | Products ^{a)} and Yields (%) ^{b)} | | | | | | | |
|------------------|---------|--------------------|---|-----|------|-----------------|------|-------|-----|------|
| | | | A | B | C | D ^{d)} | E | F | G | H |
| N-t-Butylphenyl- | MeOH | + | 7.7 | 0.9 | 5.2 | | | | | |
| " | EtOH | - | 20.5 | | | 5.6 | 41.4 | | | |
| " | " | + | 37.0 | 4.4 | 18.0 | 0.8 | 4.6 | | | |
| * " e) | " | + | 12.9 | 2.9 | 17.0 | 1.1 | 7.1 | | | |
| " f) | " | + | 12.0 | 3.5 | 14.6 | 3.4 | 17.8 | | | |
| * " } e, f) | { " | + | 2.6 | 1.1 | 7.3 | 3.1 | 15.5 | | | |
| * " } | | + | 35.6 | 3.0 | 6.8 | 0.6 | 3.4 | | | |
| " g) | " | - | 19.6 | | | 7.4 | 40.3 | | | |
| * Diphenyl- | MeOH | - | | | | | | 23.2 | | 13.7 |
| " | " | + | | | | | | trace | | |
| * " h) | EtOH | + | | | | | | 31.2 | 6.5 | |

- a) The products are represented as follows: A = N-t-butyl-aniline; B = N-t-butyl-o-chloroaniline; C = N-t-butyl-p-chloroaniline; D = N-t-butyl-o-ethoxyaniline; E = N-t-butyl-p-ethoxyaniline; F = diphenylamine; G = 4-chlorodiphenylamine; H = 4-methoxydiphenylamine.
- b) The yields are averages based on at least two identical experiments, except those marked * for which only one satisfactory set of results was obtained.
- c) The presence of LiCl in the reaction mixture is indicated by +.
- d) No authentic sample of this compound was available but its appearance on g.l.c. traces in conjunction with the p-isomer, and its mass spectrum ($M^+ = 193$) strongly support the assignment.
- e) The reaction was carried out at 65°.
- f) Two or three drops (ca 0.05 ml) of CF_3COOH were added initially to the solution of reactants.
- g) Two or three drops (ca 0.05 ml) of CH_3COOH were added initially to the solution of reactants.
- h) Several repetitions of this experiment gave only very low yields (F, ca 2% and G, ca 0.2%).

The same general method was used to deoxygenate N-t-butyl-p-tolyl nitroxide in ethanol. However g.l.c. analysis was unsatisfactory, although N-t-butyl-p-toluidine and N-t-butyl-p-tolyl hydroxylamine may have been detected.

In connection with those experiments in which CF_3COOH was added to the reaction mixture, a solution of N-t-butylaniline (0.28 g, 1.9 mmole) and CF_3COOH (0.05 ml) in ethanol (15 ml) was purged of oxygen with N_2 and boiled under reflux, under N_2 , for 64 h. Comparison by g.l.c. of the final solution with a sample of the initial solution showed that no reaction had occurred.

H. Thermolysis and Photolysis of Tetraz-2-enes

1) Thermolysis of 1,4-di-t-butyl-1,4-bisphenyltetraz-2-ene.

The tetraz-2-ene (0.05-0.59 mmole) was dissolved in dry alcohol (15-25 ml), and lithium chloride was added when required. The solution was

purged of oxygen by bubbling a stream of nitrogen through it for 10-15 min, and was then boiled under reflux, under N_2 , with stirring for 64 h. The solvent was removed in vacuo, and the residue was dissolved in a few ml of ether. An accurately weighed sample of bibenzyl was also dissolved in the ether solution to enable the yields of products to be calculated by the internal standard method, described in section G. Identification of the products was initially by g.l.c. /m. s. and subsequently by comparison of retention times with those of authentic samples.

Table 10 lists the experiments which were carried out, and products and yields which were obtained.

Table 10

Thermolysis of 1,4-di-t-butyl-1,4-bisphenyltetraz-2-ene

| Solvent | LiCl ^{c)} | Products ^{a)} and Yields (%) ^{b)} | | | | |
|---------|--------------------|---|-----|-----|-----------------|-----|
| | | A | B | C | D ^{d)} | E |
| MeOH | - | 23.7 | | | 0.7 | 2.6 |
| " | + | 24.3 | 0.2 | 2.1 | 0.3 | |
| EtOH | + | 24.4 | 0.8 | 1.7 | | |

a) The products are represented as follows: A = N-t-butylaniline; B = N-t-butyl-o-chloroaniline; C = N-t-butyl-p-chloroaniline; D = N-t-butyl-o-methoxyaniline; E = N-t-butyl-p-methoxyaniline.

b) The quoted yields are the average results of two experiments. They are calculated on the assumption that the stoichiometry of the reaction is tetrazene (1 mole) \rightarrow diphenylaminyl radicals (2 mole) \rightarrow products.

c) The presence of LiCl in the reaction mixture is indicated by +.

d) No authentic sample of this compound was available but comparison of its mass spectrum with that of authentic N-t-butyl-p-methoxyaniline (kindly provided by Dr. A. G. Rowley) strongly supports the assignment.

Thermolysis of 1,4-dimethyl-1,4-bisphenyltetraz-2-ene in

methanol saturated with LiCl gave a dark bluish-purple solution which t.l.c. showed to contain several components, but no satisfactory g.l.c. analysis could be obtained.

2) Photolysis of 1,4-di-t-butyl-1,4-bisphenyltetraz-2-ene. -

(i) The tetraz-2-ene (0.51 g, 1.57 mmole) was dissolved in dry methanol (90 ml) and the solution was purged of oxygen by passing a stream of nitrogen through it for 15 min. The stirred solution was then irradiated by means of a medium-pressure mercury lamp fitted with a pyrex filter. After 30 min the solution was examined and appeared to be evolving nitrogen. After 3 h all the starting material had reacted (t.l.c.), so an accurately weighed sample of bibenzyl was added and the solution was evaporated to a small volume to be examined by g.l.c. The yields of products, identified by g.l.c. /m.s. and comparison of retention times with authentic samples, were obtained by the internal standard method (section G), and were as follows: N-t-butylaniline, 38.1%; N-t-butyl-o-methoxyaniline, 0.7%.

(ii) The tetraz-2-ene (0.654 g, 2.02 mmole) was dissolved in dry methanol (100 ml) and LiCl (10.5 g, 0.24 mole) was added. The photo-reaction was then carried out as in (i) above, and gave the following products: N-t-butylaniline, 46.1%; N-t-butyl-p-methoxyaniline, 0.6%.

I. Miscellaneous Reaction

Deoxygenation of 2-Chlorocyclohexyl 2'-nitrophenyl Sulphide by Triethyl Phosphite.

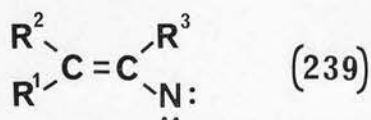
The sulphide (2.72 g, 0.01 mole) was mixed with triethyl phosphite (4.15 g, 0.025 mole). On addition of cumene (50 ml) an intense deep-red colour was produced. As the solution was heated to the boiling point the colour became pale yellow. After boiling under reflux, under N₂, for 72 h, t.l.c. examination showed that all the sulphide had reacted. However removal of solvent and chromatography of the residue on silica gave only small amounts of unidentified oils.

Discussion

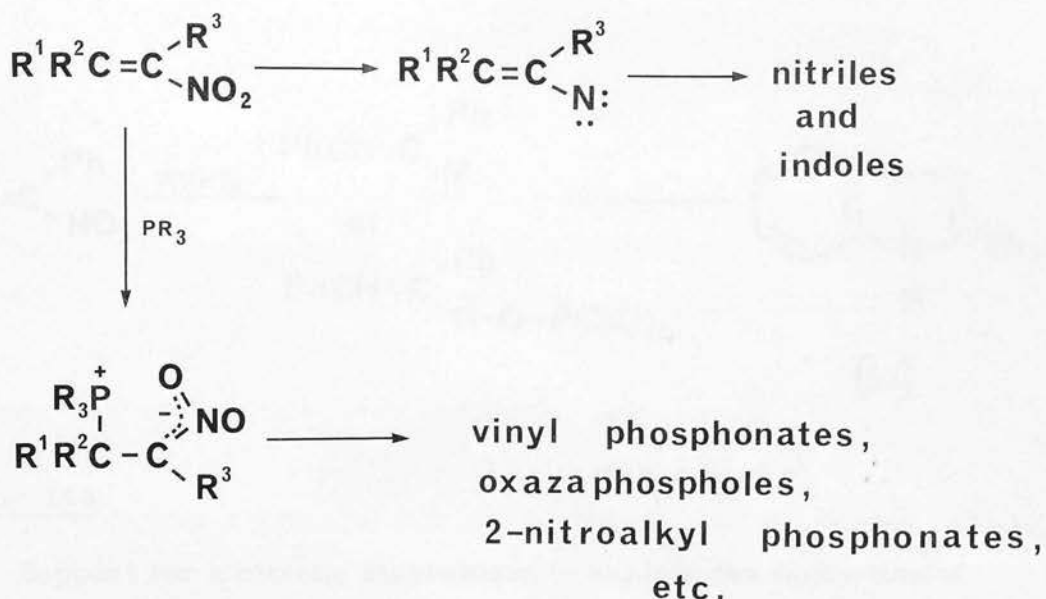
A. Reactions of 1,2-Diaryl-1-nitroethenes with Tervalent Phosphorus Reagents.

A. 1 Formation of nitrene-derived products

Whereas the deoxygenation of aryl nitro-compounds by tervalent phosphorus reagents to give products formally derived from a nitrene intermediate has received much attention (see Introduction), the possibility of using the reaction to generate vinyl nitrenes (239) has been comparatively

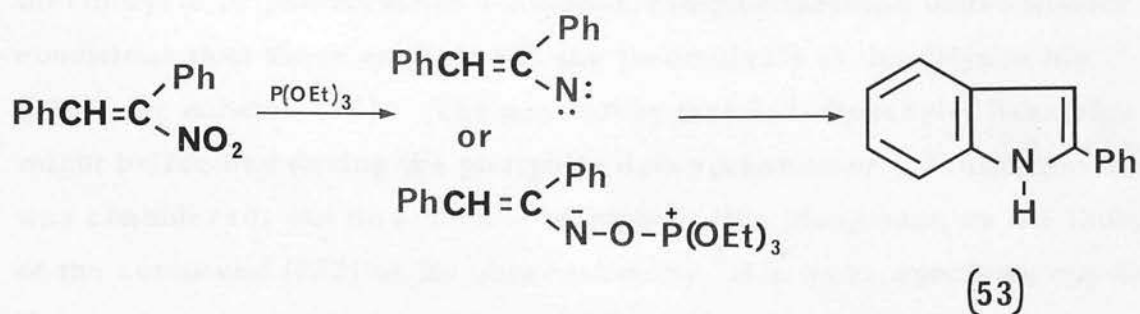


neglected. The work of Krueger,^{42, 116, 117} and Teichmann,^{118, 119} and coworkers, on the reactions of β -nitrostyrenes with tervalent phosphorus reagents and by Gareev¹¹¹⁻¹¹⁵ on the analogous reactions of simple aliphatic derivatives of nitroethene (Introduction, sections A. 2. c and B. 3) indicated that two competing pathways might operate i. e. deoxygenation of the nitro-group to give a nitrene which could subsequently rearrange to nitriles and to indoles, and Michael-type addition of the nucleophilic phosphorus reagent to the activated 2-position of the double bond leading to organophosphorus derivatives (scheme 143).



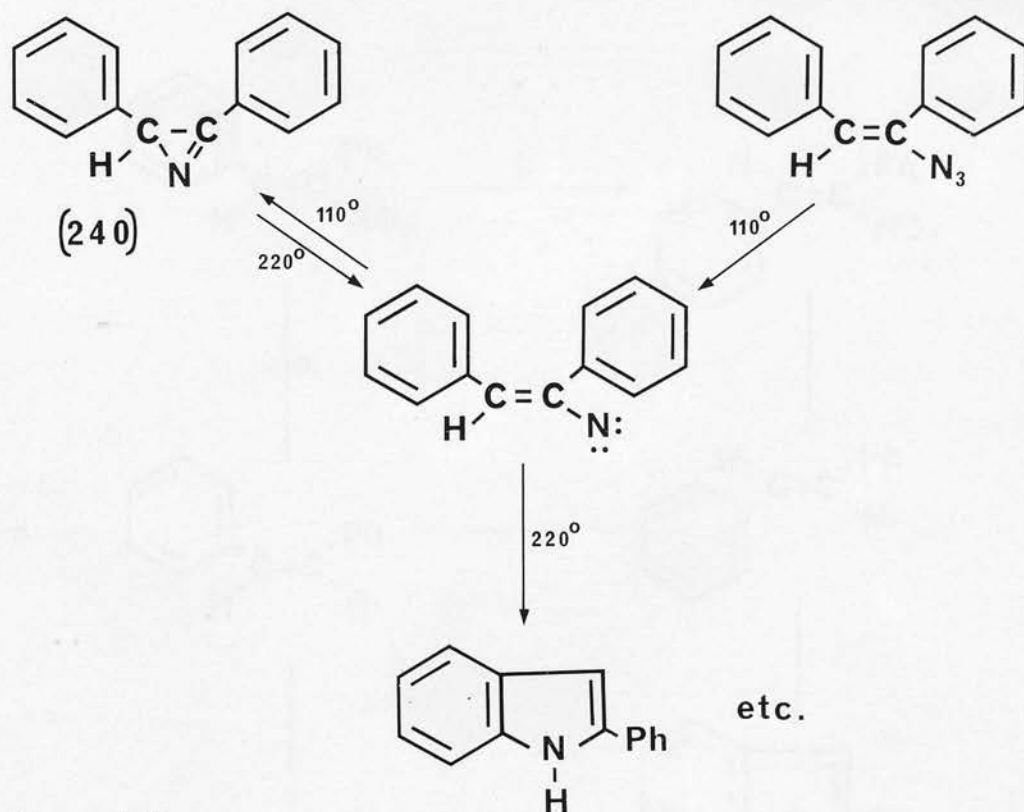
Scheme 143

It was proposed that a study of the reactions of 1,2-diaryl-nitroethenes with triethyl phosphite should be carried out, in the hope of discovering conditions more favourable towards the formation of nitrene-derived products. It was already known that reaction of 1,2-diphenylnitroethene (α -nitrostilbene) with boiling triethyl phosphite gave 2-phenylindole (53; 16%), probably by a nitrene or nitrenoid mechanism,³⁴ (scheme 144) and this was a convenient reference from which to start the investigation.



Scheme 144

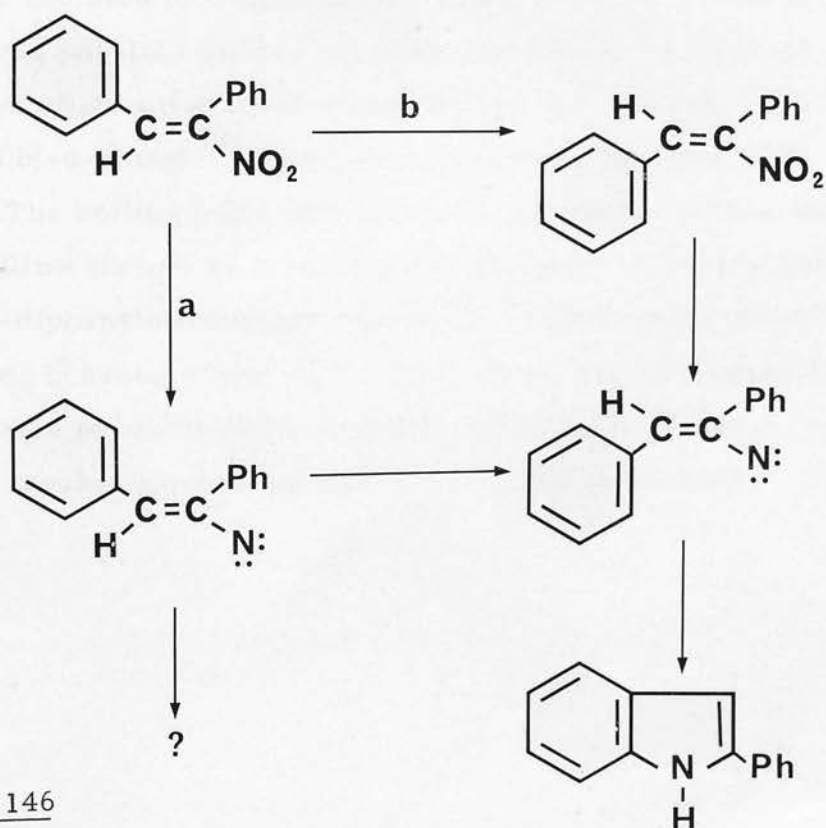
Support for a nitrene mechanism to explain the formation of 2-phenylindole came from studies of the decomposition of 2,3-diphenyl-2H-azirine (240; scheme 145). It is generally agreed that a major decomposition pathway of the 2H-azirine (240) is via the vinyl nitrene¹⁷⁵ and indeed it has been suggested that 2H-azirines may exist in equilibrium with the vinyl nitrene.¹⁷⁶ Many products have been isolated from the thermolysis of 2,3-diphenyl-2H-azirine, but a major product is 2-phenylindole (37-63 %), although 2H-azirines are also prone to polymerise.¹⁷⁷



Scheme 145

The 2H -azirine (240) is prepared¹⁷⁸ via the nitrene by thermolysis or photolysis of 1-azido-1,2-diphenylethene under milder conditions than those employed in the thermolysis of the 2H -azirine (240) (see scheme 145). The possibility that 2,3-diphenyl- 2H -azirine might be formed during the phosphite deoxygenation of 1,2-diphenylnitroethene was considered, but no evidence to support this idea, such as the isolation of the compound (240) or its observation by ^1H n. m. r. spectroscopy during the course of the reaction (see section A.3), was obtained.

It has been shown^{140,179} that the configuration of the double bond of 1,2-diphenylnitroethene is E, i.e. the phenyl groups are cis to each other. Because the nitrene derived from E-1,2-diphenylnitroethene would be trans to the group into which it must insert to form 2-phenylindole, isomerisation of the double bond would have to occur at some stage in the reaction. Either the trans-nitrene was formed first and a small proportion isomerised to give the cis-nitrene and hence 2-phenylindole, while the greater part reacted to give intractable material, or, alternatively, a certain amount of isomerisation of the 1,2-diphenylnitroethene occurred before deoxygenation, so that the cis-nitrene was formed directly (scheme 146). The observation that when the reaction was carried out in decalin



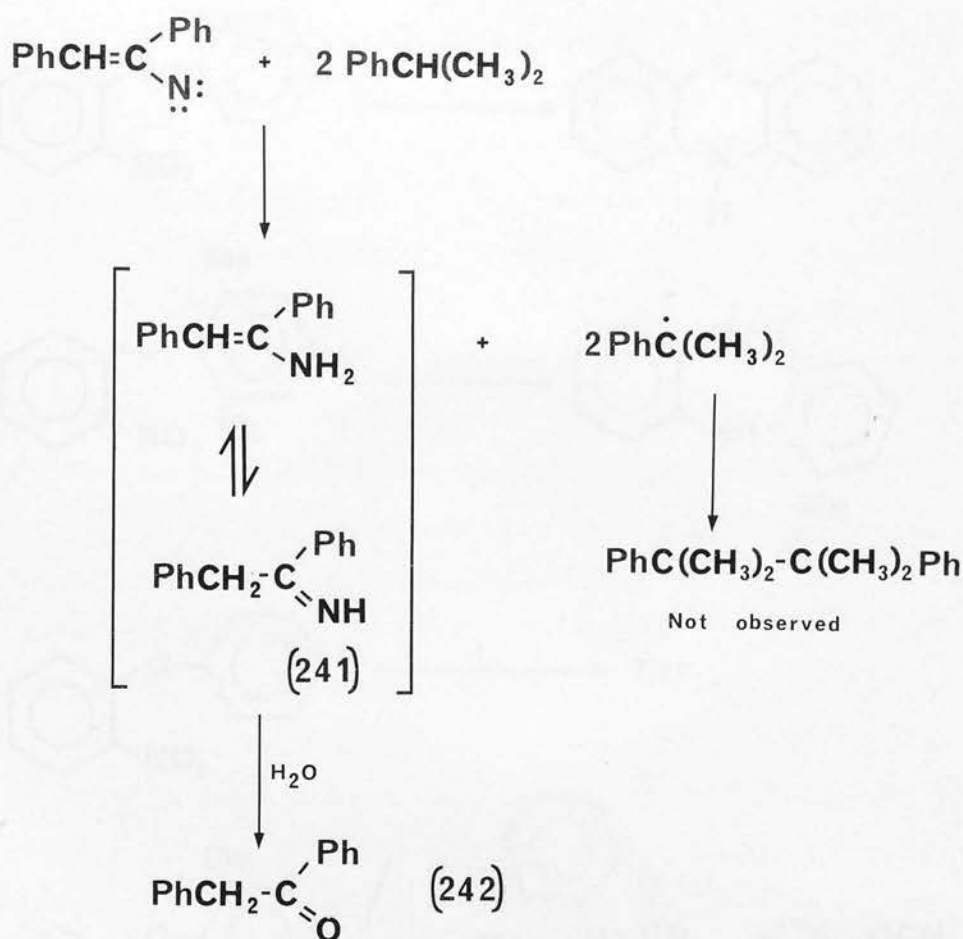
Scheme 146

at 190° [cf. 165° for (EtO)₃P], a slightly improved yield (18%) of 2-phenylindole was obtained, seemed to support the notion that thermal double-bond isomerisation was a factor in determining the poor yields of product.

To test this theory, Z-1,2-diphenylnitroethene was prepared by the photolysis of an ethanolic solution of the E-isomer and was subjected to the same deoxygenation conditions as those used to obtain 2-phenylindole from E-1,2-diphenylnitroethene. In this way a nitrene in the more appropriate configuration ought to be obtained directly, eliminating the necessity of a double-bond isomerisation. 2-Phenylindole was indeed obtained again, but in only 8% yield, thus failing to substantiate the theory. The stereochemistry of the 1,2-diarylnitroethenes is of further relevance in connection with their cyclo-addition to phosphites and phosphonites, and this is discussed below in section A.4.

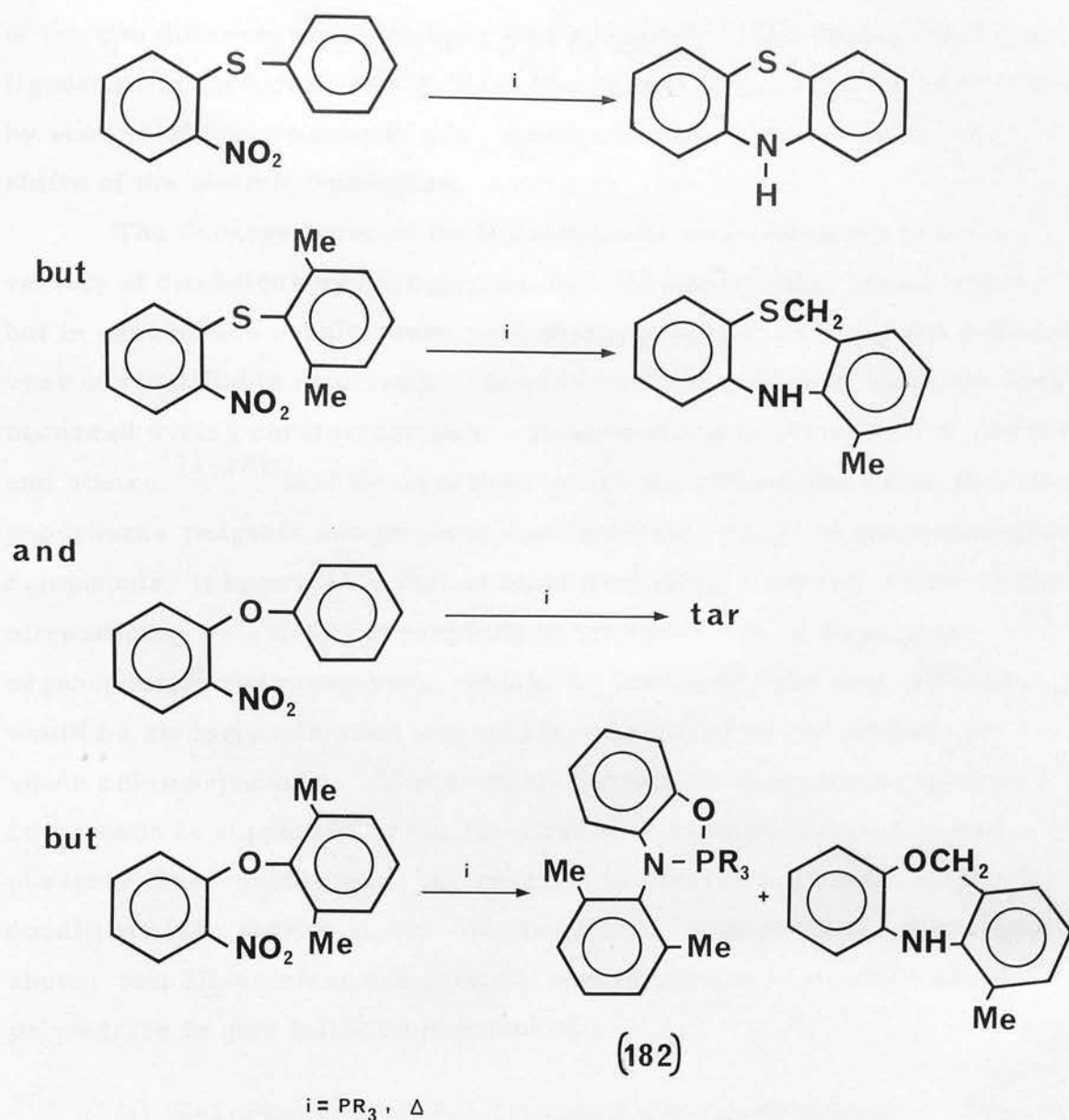
The use of a solvent in phosphite deoxygenation reactions has been found to improve yields in cases where a heterocyclic system is formed (phenothiazines in particular^{50c}). In addition to the use of decalin as solvent for the deoxygenation of 1,2-diphenylnitroethene, with the resulting small improvement in yield described above, cumene, a common solvent for this reaction, was tried. The only product which could be isolated in this case, however, was deoxybenzoin (242; 10%), which was possibly formed by hydrolysis of an imine (241), the product of hydrogen abstraction by the nitrene from the solvent. No solvent-derived bi- α -cumyl^{50c} was found, however, (scheme 147).

The boiling point of benzene is generally considered to be too low to allow its use as a solvent for phosphite deoxygenation reactions, but 1,2-diphenylnitroethene reacted completely with triethyl phosphite in boiling benzene within 42 hours. However, no 2-phenylindole or other identifiable products were obtained, which casts doubt on whether a nitrene mechanism can operate under these conditions.



Scheme 147

In previous investigations Cadogan has found that the "blocked-ortho" effect is often useful in diverting a previously unproductive or routine reaction to give unexpected products.⁵ For example, deoxygenation of 2-nitrophenyl phenyl sulphide gives phenothiazine whereas 2-nitrophenyl 2,6-dimethylphenyl sulphide gives 5,11-dihydro-4-methyl-dibenz[b,e][1,4]thiazepine. The corresponding diaryl ethers give tar, and a 1,3,2-benzoxazaphosph(v)ole (182), respectively (scheme 148).



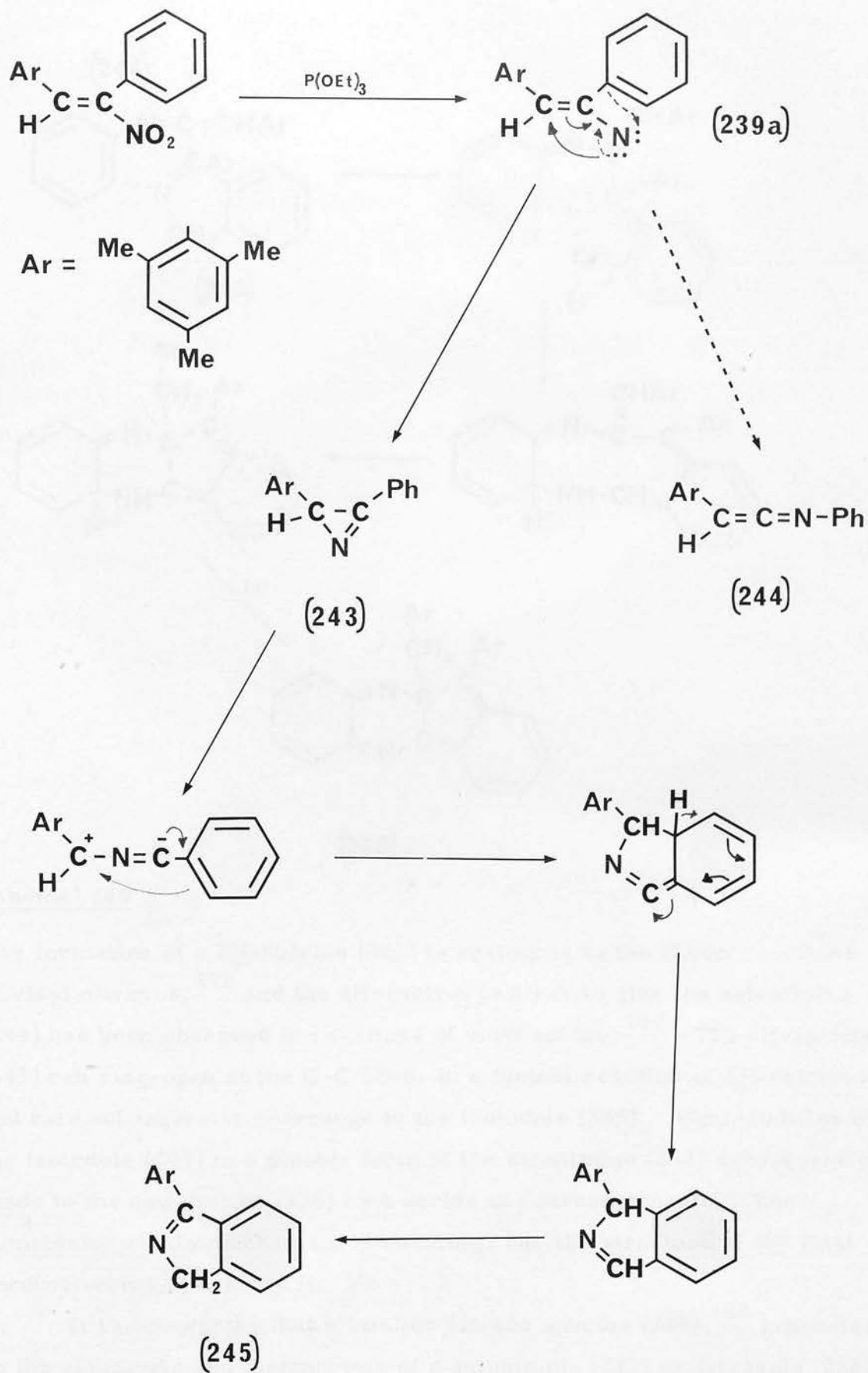
Scheme 148

It was decided to investigate the blocked-ortho effect in a series of 1,2-diarylnitroethenes by studying several compounds in which the 2-aryl group was 2',6'-disubstituted, hence blocking a favoured route to indole formation. The following compounds were successfully prepared by the standard method of Robertson¹³⁸ (Experimental section B. 2): 2(2',6'-dichlorophenyl)-, 2(2',4',6'-trimethylphenyl)-, and 2(2',4',6'-trimethoxyphenyl)-1-phenyl-1-nitroethenes. In addition,

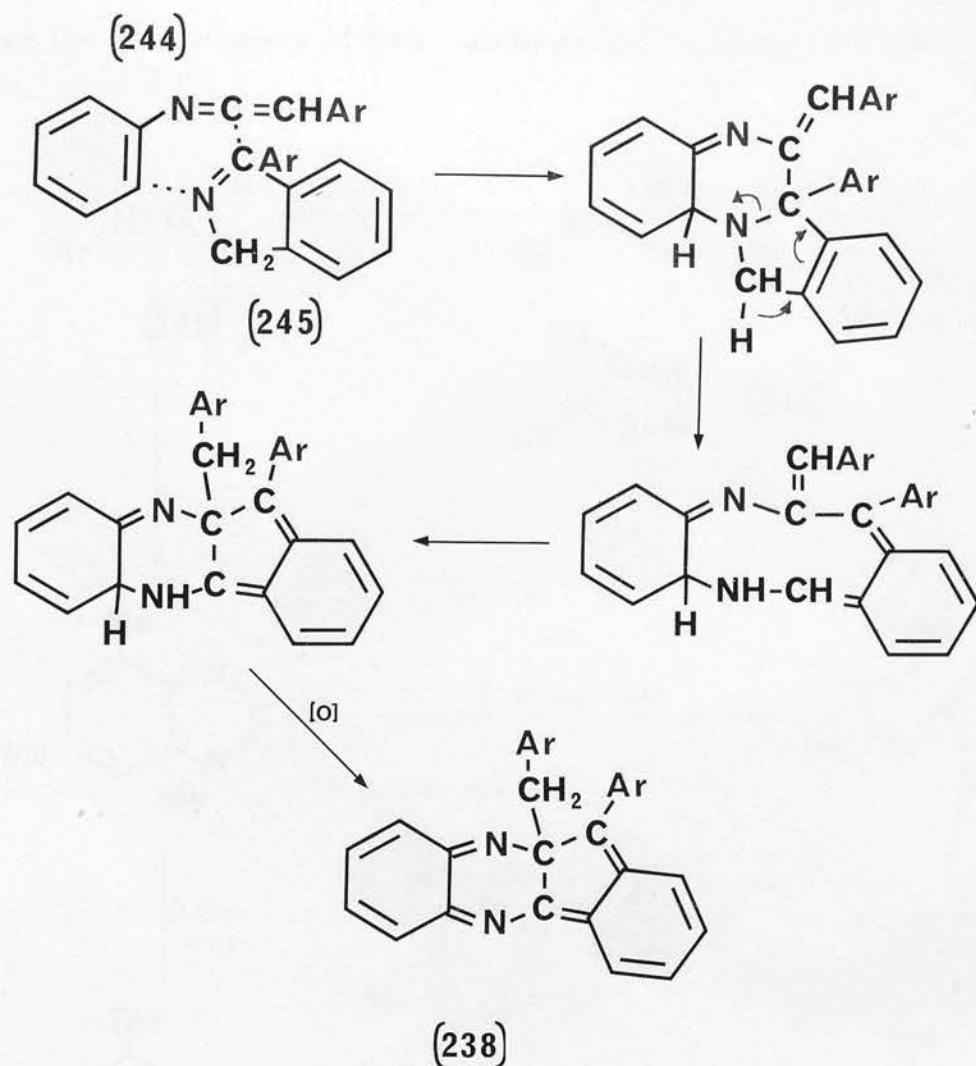
2(2'-nitrophenyl)-1-phenyl-1-nitroethene, potentially of interest because of the two different nitro-groups, was prepared. The double-bond configuration in each case was E, i.e. the phenyl groups cis, as determined by studies of the compounds' u. v. spectra and the n. m. r. chemical shifts of the olefinic hydrogens.

The deoxygenation of these compounds was attempted under a variety of conditions by changing the solvent and reaction temperature, but in general the results were very disappointing because of the poor recovery of identifiable materials. In each case the principal material loss occurred during chromatography. In view of the observations of Gareev and others¹¹¹⁻¹²¹ that the reactions of simple nitroethenes with trivalent phosphorus reagents can produce a considerable range of organophosphorus compounds, it is probable that at least part of the material deficit in the nitrostilbene reactions corresponds to the formation of analogous organophosphorus compounds, which, by nature of their high polarity, would be strongly adsorbed and slowly hydrolysed by the alumina or silica column-packing. The probable formation of organophosphorus compounds is supported by the isolation of 4,5-dihydro-1,2,5-oxazaphosph(v)ole-2-oxides when the reaction is carried out under milder conditions (see section A. 2). There is also the possibility, discussed above, that 2H-azirines are formed, and that these compounds could polymerise to give intractable materials.

(i) E-1-Phenyl-2-(2,4,6-trimethylphenyl)nitroethene. - Deoxygenation of this compound by triethyl phosphite, without solvent or in benzene, t-butylbenzene, or decalin, gave 10a-(2,4,6-trimethylbenzyl)-11-(2,4,6-trimethylphenyl)-10aH-isoindeno[1,2-b]quinoxaline (238) in small yield (0.9-5.6%). This compound is formally an oxidised dimer of the nitrene derived from the title nitroethene, but the structure, which was determined by n. m. r. and mass-analysed ion kinetic spectroscopy (see Experimental section C. 3), indicates extensive molecular rearrangements. A proposed mechanism (scheme 149) involves the initial formation of a vinyl nitrene (239a) which can react intramolecularly by two routes.



(cont.)

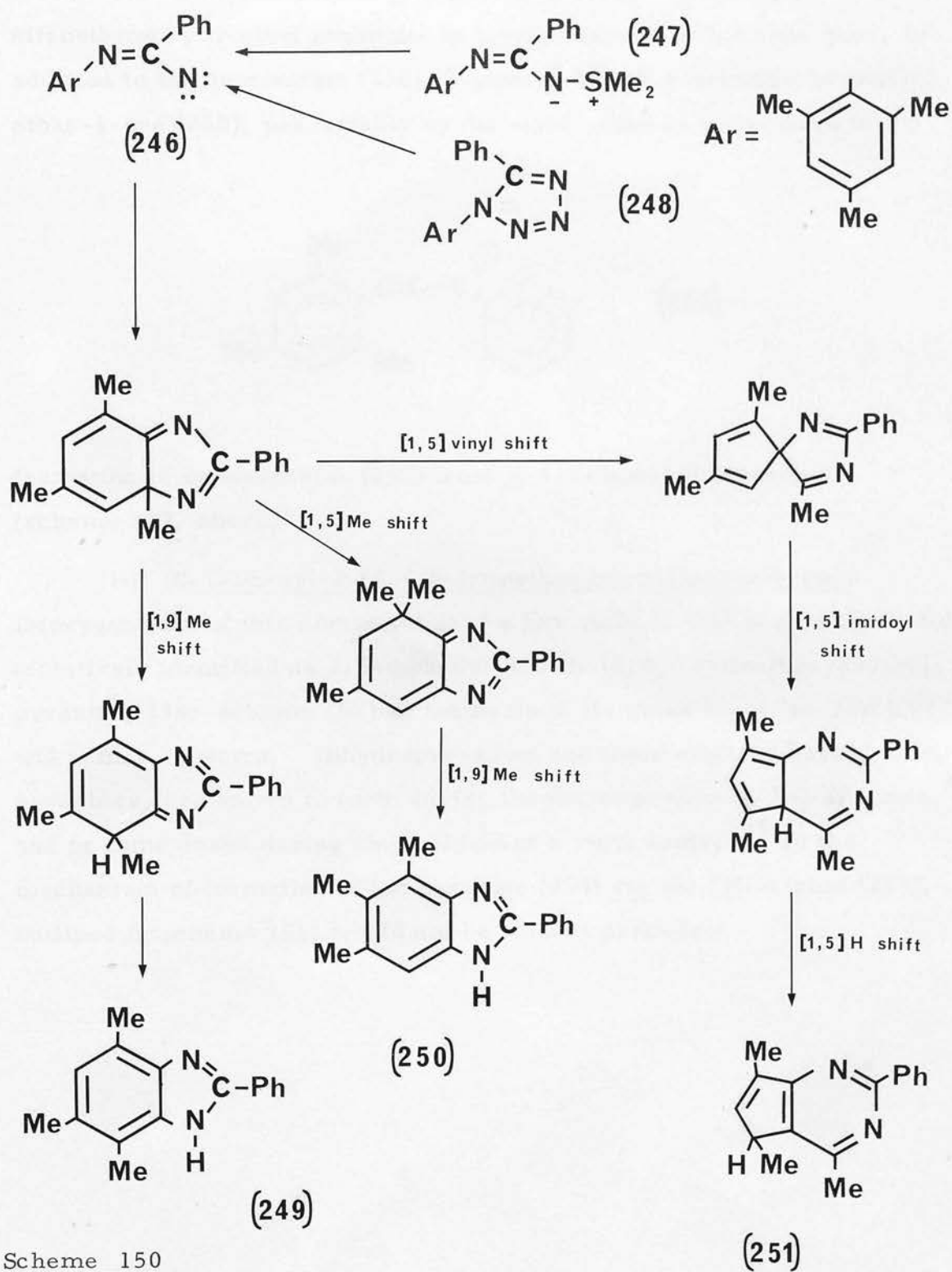


Scheme 149

The formation of a $2H$ -azirine (243) is analogous to the known reactions of vinyl nitrenes,¹⁷⁸ and the alternative pathway to give the ketenimine (244) has been observed in reactions of vinyl azides.¹⁸⁰ The $2H$ -azirine (243) can ring-open at the C-C bond, in a typical reaction of $2H$ -azirines,¹⁸¹ and may subsequently rearrange to the isoindole (245). Cycloaddition of the isoindole (245) to a dipolar form of the ketenimine (244) subsequently leads to the quinoxaline (238) by a series of rearrangements. The complexity of this mechanism is daunting, but the structure of the final product seems to demand it.

It is noteworthy that a similar nitrene species (246),¹⁸² generated by the photolysis and thermolysis of a sulphimide (247) or tetrazole (248)

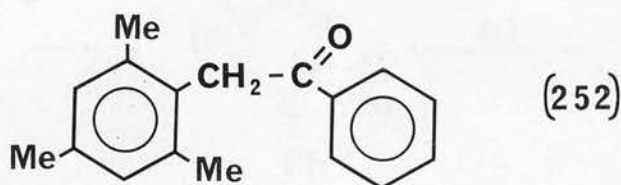
apparently follows the reaction pathway which one might have expected for the vinyl nitrene (239a). In this case (scheme 150) the nitrene (246)



Scheme 150

attacks the blocked ortho position of the 2-aryl ring and a sequence of novel rearrangements occurs to give benzimidazoles (249, 250) and a pyrimidine (251).

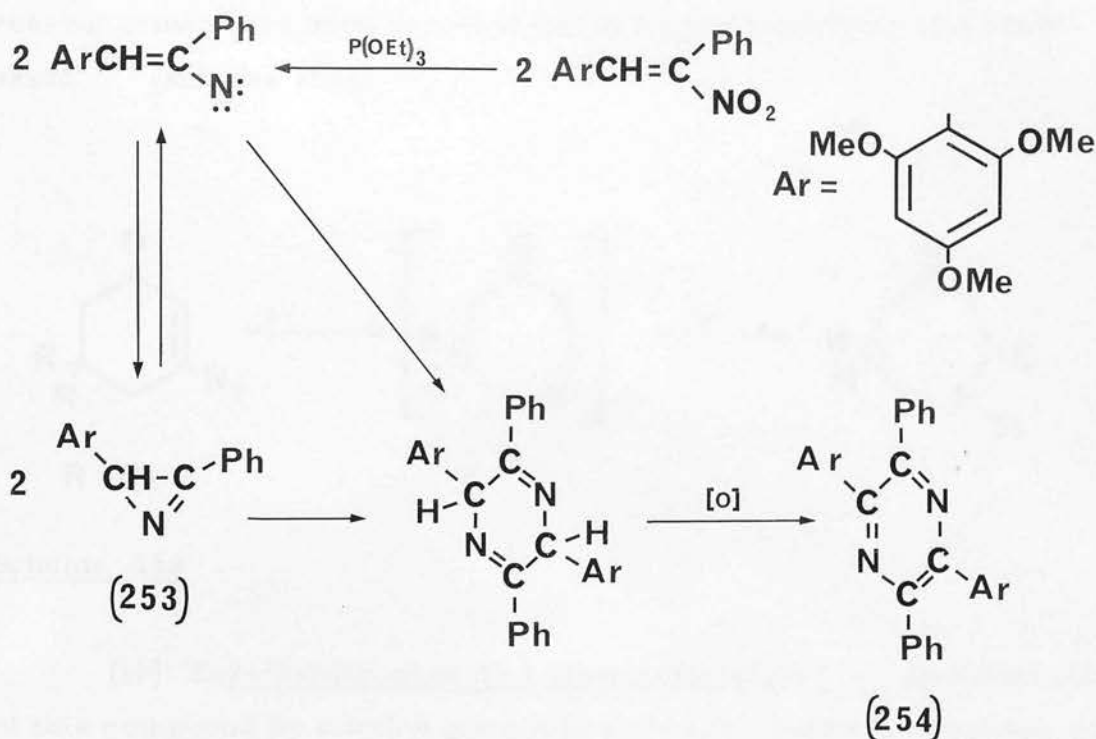
The deoxygenation of E-1-phenyl-2-(2,4,6-trimethylphenyl)-nitroethene by triethyl phosphite in t-butylbenzene or benzene gave, in addition to the quinoxaline (238), 1-phenyl-2-(2,4,6-trimethylphenyl)-ethan-1-one (252), presumably by the same route as is involved in the



formation of deoxybenzoin (242) from E-1,2-diphenylnitroethene (scheme 147, above).

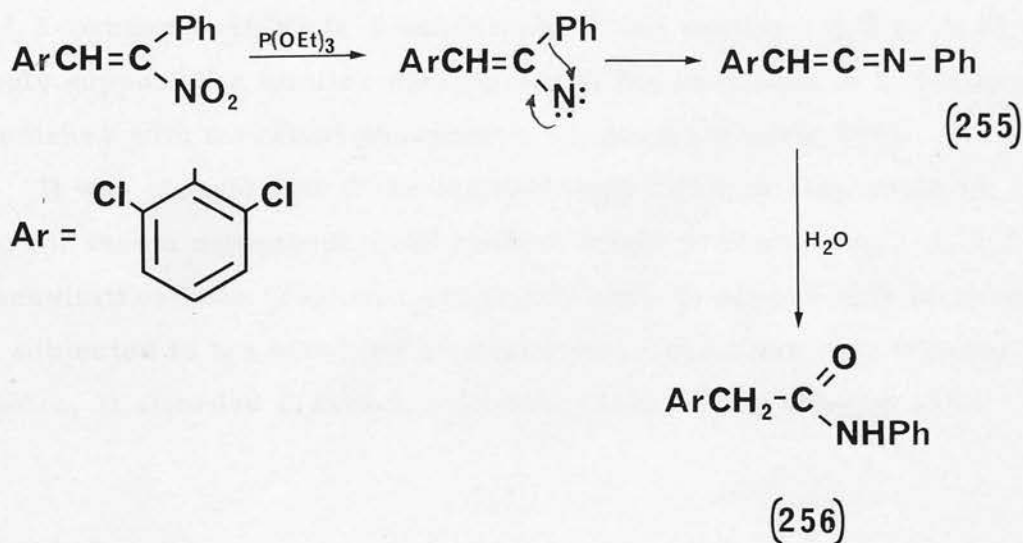
(ii) E-1-Phenyl-2-(2,4,6-trimethoxyphenyl)nitroethene. -

Deoxygenation of this compound gave a low yield (1.4%) of a yellow solid, tentatively identified as 2,5-diphenyl-3,6-di-(2,4,6-trimethoxyphenyl)-pyrazine (254; scheme 151) on the basis of its mass spectrum and i. r. and n. m. r. spectra. Dihydropyrazines and their oxidised derivatives, pyrazines, are known to form during the decomposition of 2H-azirines,^{180a, 181} and in some cases during thermolysis of a vinyl azide,¹⁸⁴ so the mechanism of formation of the pyrazine (254) via the 2H-azirine (253), outlined in scheme 151, would not be without precedent.



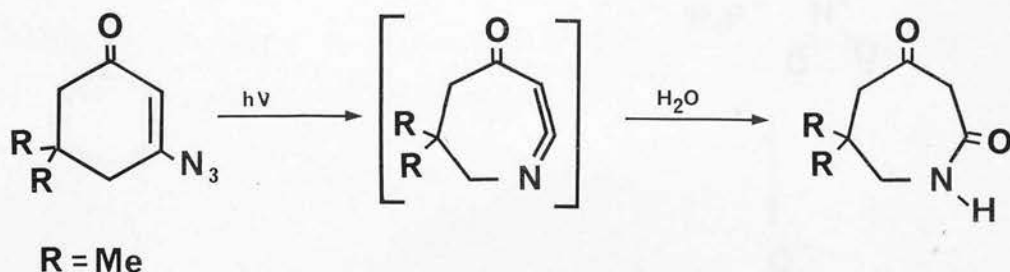
Scheme 151

(iii) E-1-Phenyl-2-(2,6-dichlorophenyl)nitroethene. - Deoxygenation of this compound by triethyl phosphite gave only triethyl phosphate (69%) when the reaction was carried out in decalin, but when benzene was the solvent 2-(2,6-dichlorophenyl)-N-phenylacetamide (256; 2.9%) was obtained. This may have been formed by hydrolysis of the ketenimine (255; scheme 152). A similar reaction involving the same Curtius-type



Scheme 152

rearrangement has been reported following the photolysis of a vinyl azide¹⁸⁵ (scheme 153).

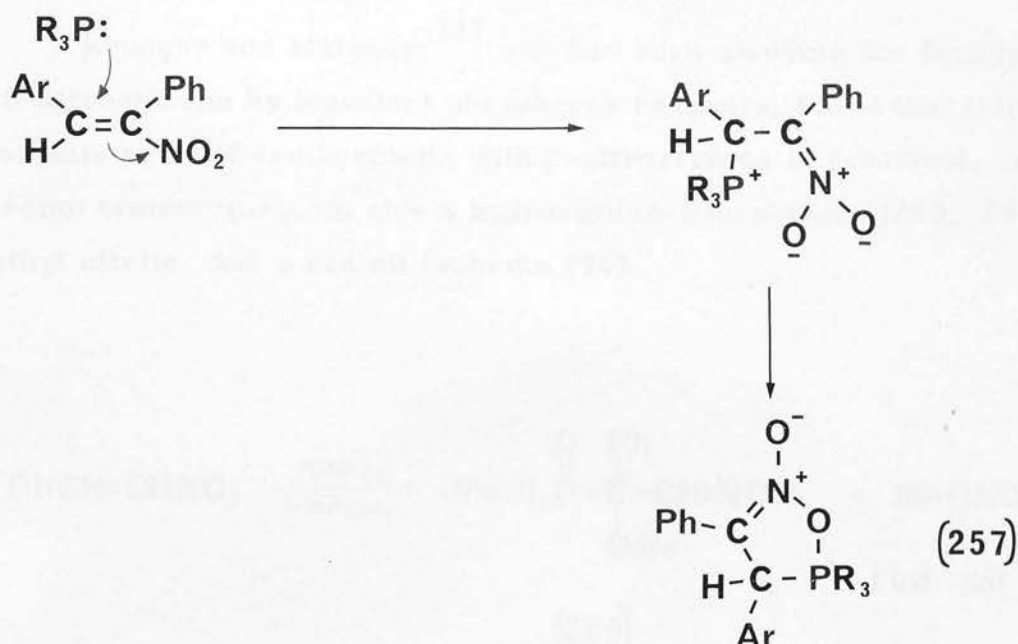


Scheme 153

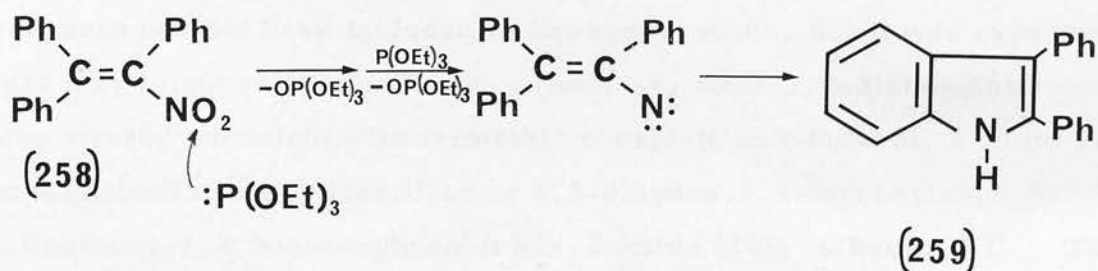
(iv) E-2-(2-Nitrophenyl)-1-phenylnitroethene. - Deoxygenation of this compound by triethyl phosphite gave two unidentified solids, each in low yield (less than 4%). Examination of the n. m. r. and mass spectra of these products failed to give sufficient information for identification of their structure.

The failure to improve the yields of nitrene-derived products by the attempts described above - inversion of double-bond configuration, dilution in a solvent, and the blocked-ortho effect - prompted a different approach to the study of the reactions of 1,2-diarylnitroethenes. Gareev, and others,¹¹¹⁻¹²¹ had shown that Michael-type addition of the tervalent phosphorus reagent to the double bond of a nitroethene was a viable reaction pathway and the isolation and observation by n. m. r. spectroscopy of 1,2,5-oxazaphosph(v)ole-2-oxides (257) (see sections A. 2 to A. 4) strongly supported a similar mechanism in the reactions of 1,2-diaryl-nitroethenes with tervalent phosphorus reagents (scheme 154).

It was thought that if the Michael-type addition step could be hindered, then a nitrene-derived product might predominate. 1,2,2-Triphenylnitroethene (258) was prepared, and, in accord with expectation, when subjected to the standard deoxygenating conditions with triethyl phosphite, it afforded 2,3-diphenylindole (259, 70%) (scheme 155).



Scheme 154



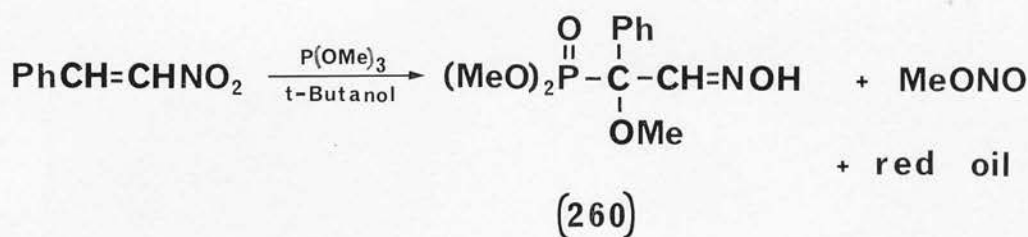
Scheme 155

The additional phenyl group can hinder the Michael-type addition pathway in two ways - by simple steric hindrance to the incoming nucleophile, and by disrupting the planarity of the molecule so that delocalisation of positive charge onto the 2-position of the double bond is reduced. The latter reason is probably the more important of the two, and is considered further in section A. 4.

Thus the good yield of 2,3-diphenylindole obtained from 1,2,2-triphenylnitroethene opens up potential new avenues of research into the reactions of vinyl nitrenes generated by the nitro/phosphite reaction.

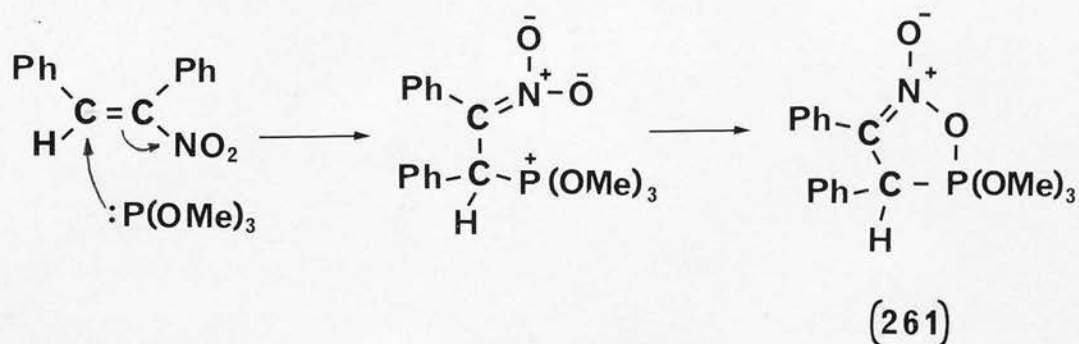
A. 2 Formation of 1,2,5-oxazaphosph(v)ole-2-oxides.

Krueger and Maloney,¹¹⁷ who had been studying the deoxygenation of β -nitrostyrene by tervalent phosphorus reagents, found that trimethyl phosphite reacted exothermally with β -nitrostyrene in t-butanol, initially at room temperature, to give a hydroximino-phosphonate (260; 34%), methyl nitrite, and a red oil (scheme 156).



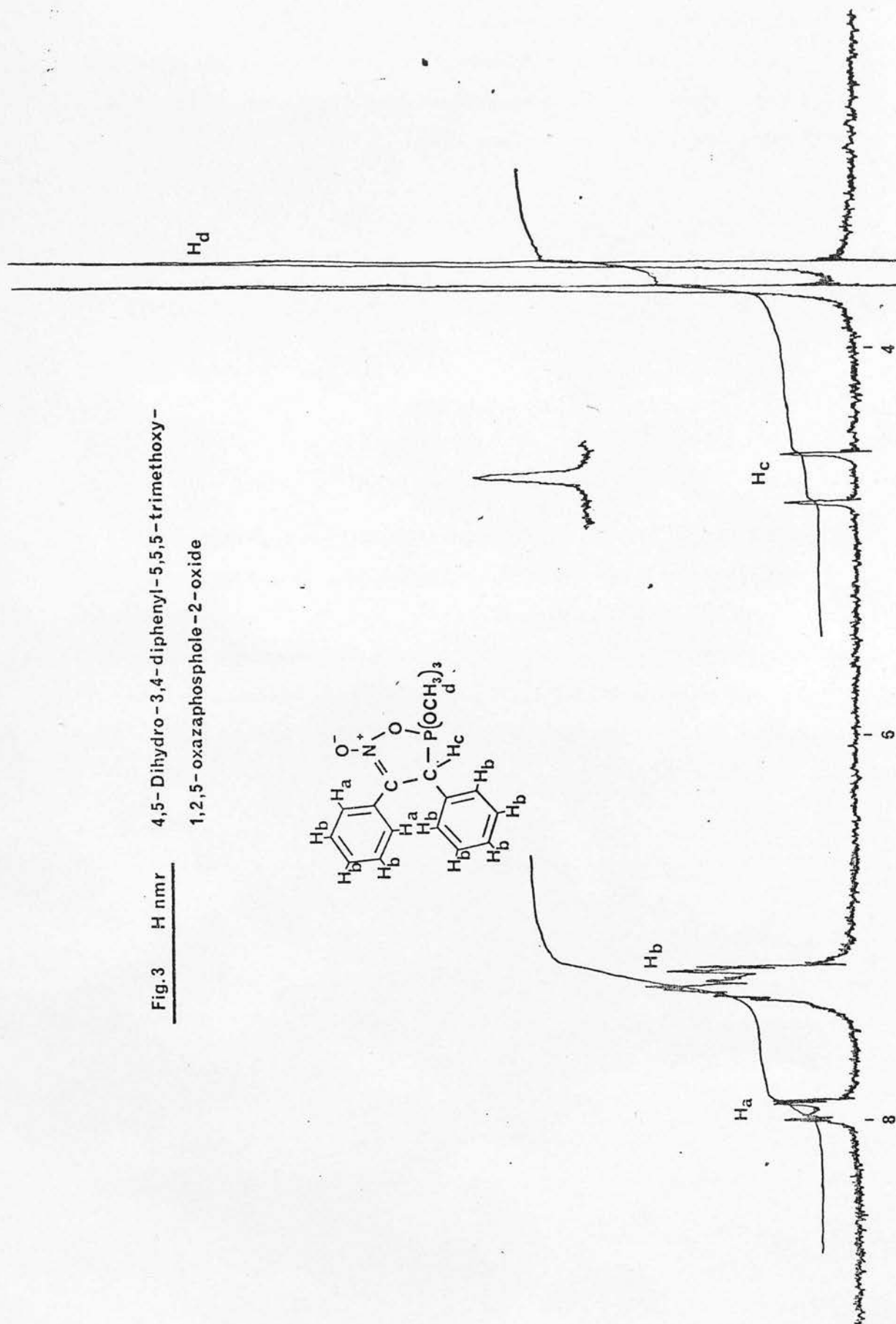
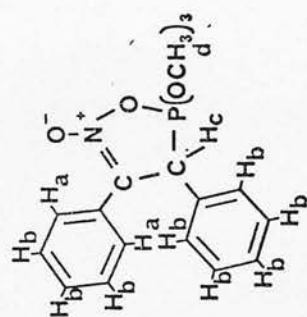
Scheme 156

The reactions of 1,2-diarylnitroethenes with tervalent phosphorus reagents had not been included in Krueger's study, but it was expected that they might react similarly. However, when 1,2-diphenylnitroethene was stirred overnight with trimethyl phosphite in t-butanol, a white solid precipitated and was identified as 4,5-dihydro-3,4-diphenyl-5,5,5-trimethoxy-1,2,5-oxazaphosph(v)ole-2-oxide (261; scheme 157). This



Scheme 157

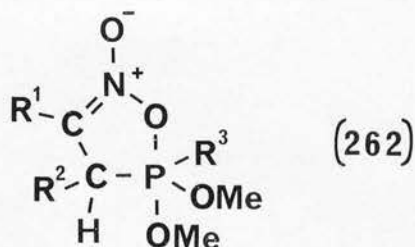
Fig.3 H nmr
4,5-Dihydro-3,4-diphenyl-5,5,5-trimethoxy-
1,2,5-oxazaphosphole-2-oxide



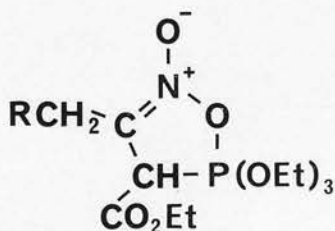
compound is a further example of a 1,2,5-oxazaphosph(v)ole-2-oxide prepared by the reaction of a tervalent phosphorus reagent with a nitroethene. Gareev^{111,113} and Shin^{120,121} have already reported examples of this ring structure, but whereas Gareev's compounds (262) are hydrolytically unstable,¹¹³ the 1,2,5-oxazaphosph(v)ole-2-oxide

a; $R^1 = \text{Me}, R^2 = \text{Me},$
 $R^3 = \text{OMe}$

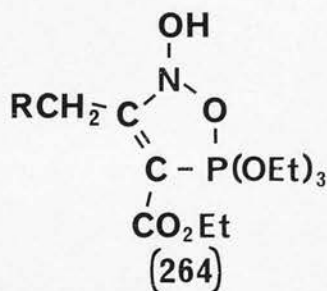
b; $R^1 = \text{H}, R^2 = \text{CH}(\text{CH}_3)_2$
 $R^3 = \text{Ph}$



(261) is readily prepared in 85% yield under conditions which do not require to be rigorously anhydrous. Shin reported that the 1,2,5-oxazaphosph(v)ole-2-oxides (263) were obtained as a mixture with the N-hydroxide (264), an example of tautomerism which was not observed in the case of 4,5-dihydro-3,4-diphenyl-5,5,5-trimethoxy-1,2,5-oxazaphosph(v)ole-2-oxide (261), or its substituted derivatives.



(263) $R = \text{CH}_3, \text{CH}_3\text{CH}_2$



In a repetition of Krueger's work,¹¹⁷ trimethyl phosphite was added to β -nitrostyrene in *t*-butanol, but the temperature was kept at 20° by external cooling. However, even under these controlled conditions, no 1,2,5-oxazaphosph(v)ole-2-oxide was obtained.

The structure of 4,5-dihydro-3,4-diphenyl-5,5,5-trimethoxy-1,2,5-oxazaphosph(v)ole-2-oxide was confirmed by n. m. r. spectroscopy. The proton n. m. r. spectrum (Figure 3) shows four distinct groups of

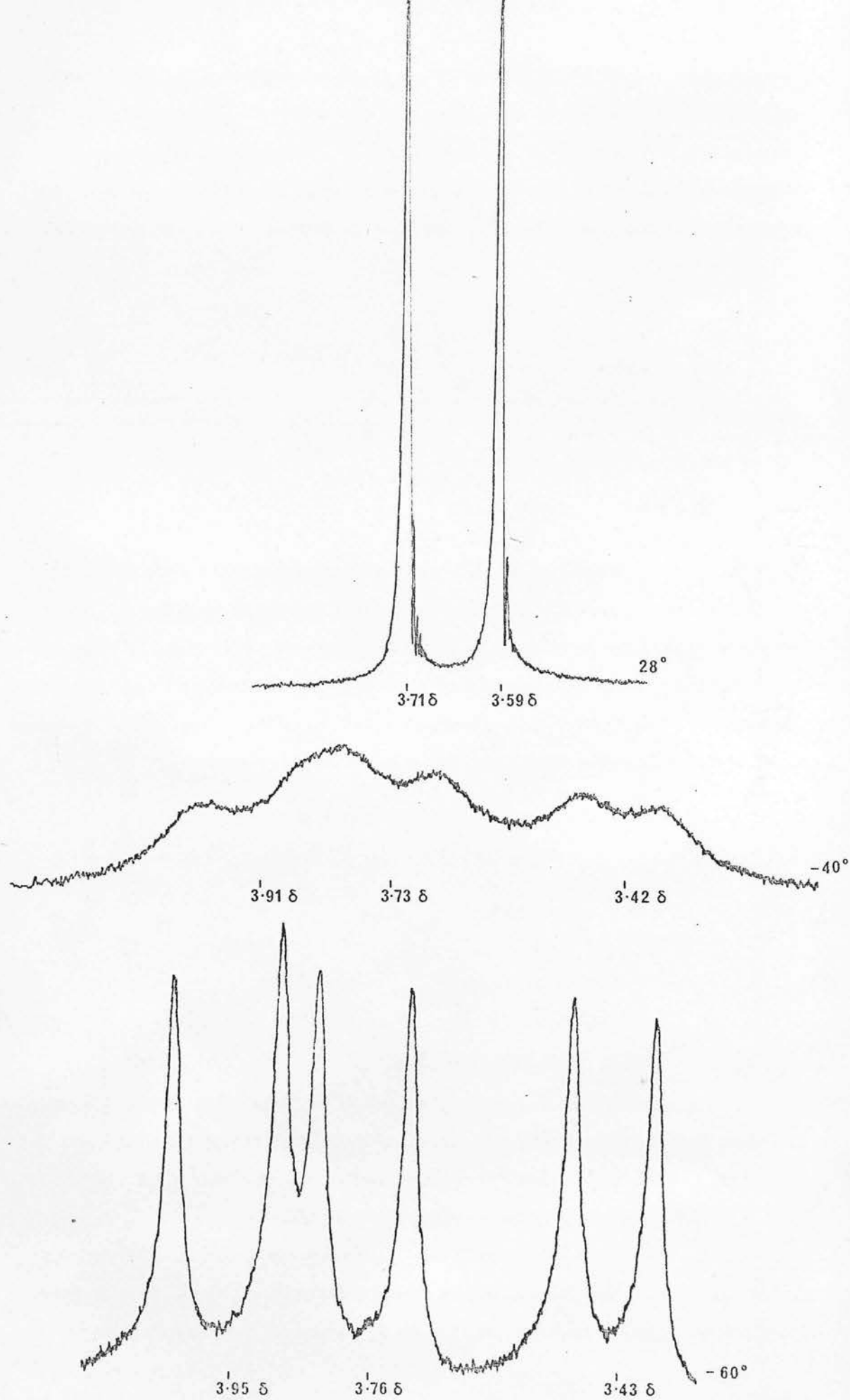


Fig.4 $^1\text{H-nmr}$ 4,5-Dihydro-3,4-diphenyl-5,5,5-trimethoxy-1,2,5-oxazaphosphole-2-oxide :-
Variable temperature study of methoxy- signals

signals, assigned as indicated in the figure. The absorptions of the nine methoxy hydrogens and the single 4-hydrogen are doublets, caused by coupling of the protons with the phosphorus nucleus. Decoupling of the doublet of the 4-hydrogen is illustrated in the figure. Two of the aromatic protons are shifted downfield relative to the others by their spatial proximity to the C=N double bond. Pseudorotation of groups about the phosphorus atom (described in the Introduction, section B. 1) means that, at room temperature, only one signal (a doublet) is observed for the three methoxy-groups. However, at a lower temperature (-60°) pseudorotation is sufficiently restricted to permit the observation of three doublets (Figure 4), corresponding to the apical methoxy-group and the two non-equivalent equatorial methoxy-groups, one of which is cis, and the other trans, to the 4-phenyl group (Figure 5).

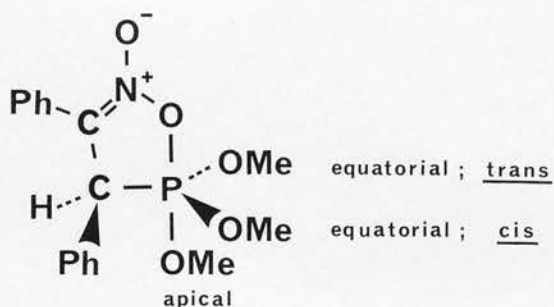


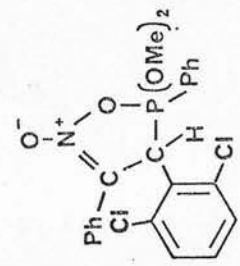
Figure 5

The ^{31}P n. m. r. spectrum shows one signal at -36.6 p. p. m. (CDCl_3), -38.9 p. p. m. (C_6D_6), which is a typical and characteristic absorption frequency for pentaco-ordinate phosphorus species.

By varying the 1,2-diarylnitroethene and the tervalent phosphorus reagent, a range of fourteen new 1,2,5-oxazaphosph(v)ole-2-oxides was prepared by a standard method. This is described in Experimental section E. 1, and Tables 5 and 6 list the new compounds. The n. m. r. spectra of these compounds (Tables 7 and 8) support the assigned structure, but several interesting features warrant further comment.

The 1,2,5-oxazaphosph(v)ole-2-oxides derived from dimethyl phenylphosphonite (compounds H to K, Table 6) offer an opportunity for diastereoisomerism. Referring to Figure 6, one can see that the 5-phenyl and 4-aryl group can exist in a cis or trans configuration.

Fig.7 P-nmr 4-(2,6-Dichlorophenyl)-4,5-dihydro-5,5-dimethoxy-3,5-diphenyl-1,2,5-oxazaphosphole-2-oxide



-33.6 ppm

0 ppm

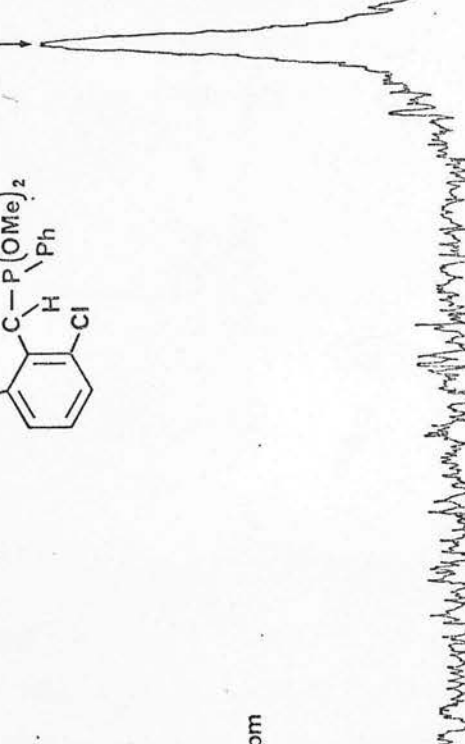
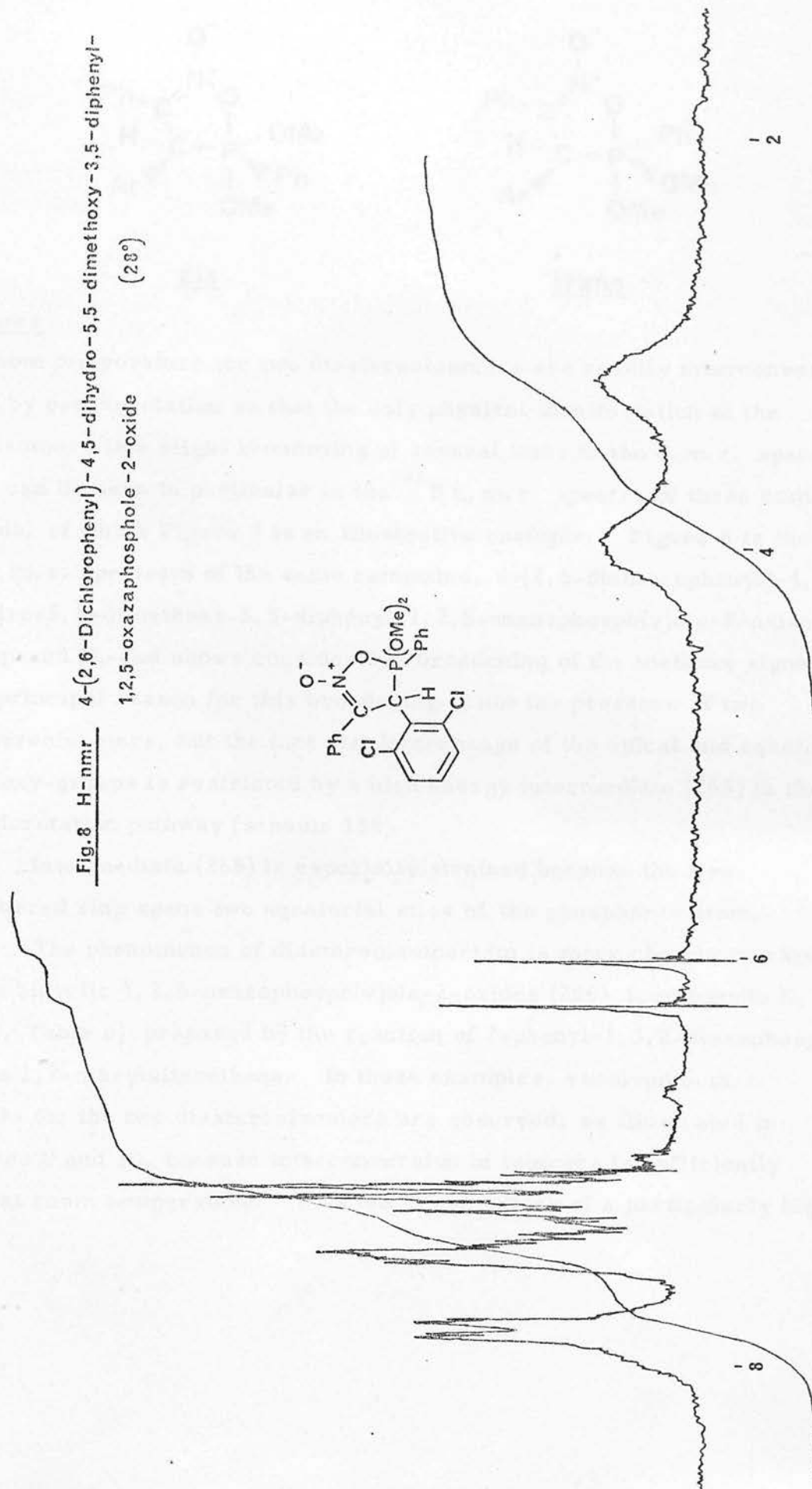
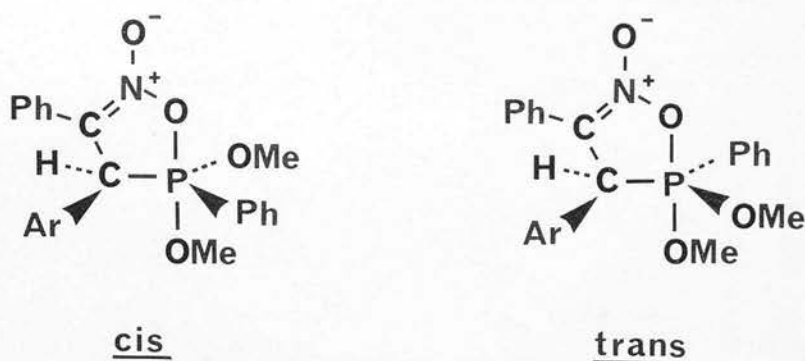


Fig. 8 H-nmr 4-(2,6-Dichlorophenyl)-4,5-dihydro-5,5-dimethoxy-3,5-diphenyl-1,2,5-oxazaphosphole-2-oxide (28°)



**Figure 6**

At room temperature the two diastereoisomers are readily interconvertible by pseudorotation so that the only physical manifestation of the two isomers is a slight broadening of several lines in the n. m. r. spectra. This can be seen in particular in the ^{31}P n. m. r. spectra of these compounds, of which Figure 7 is an illustrative example. Figure 8 is the ^1H n. m. r. spectrum of the same compound, 4-(2,6-dichlorophenyl)-4,5-dihydro-5,5-dimethoxy-3,5-diphenyl-1,2,5-oxazaphosph(v)ole-2-oxide (compound I), and shows considerable broadening of the methoxy signals. The principal reason for this broadening is not the presence of two diastereoisomers, but the fact that interchange of the apical and equatorial methoxy-groups is restricted by a high energy intermediate (265) in the pseudorotation pathway (scheme 158).

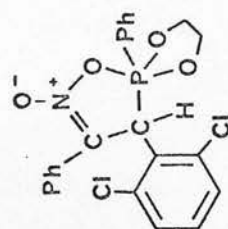
Intermediate (265) is especially strained because the five-membered ring spans two equatorial sites of the phosphorus atom.

The phenomenon of diastereoisomerism is more clearly marked in the bicyclic 1,2,5-oxazaphosph(v)ole-2-oxides (266) (compounds L, M, N, Table 6) prepared by the reaction of 2-phenyl-1,3,2-dioxaphospholan with a 1,2-diarylnitroethene. In these examples, resolved n. m. r. signals for the two diastereoisomers are observed, as illustrated in Figures 9 and 10, because interconversion of isomers is sufficiently slow at room temperature. It is the intermediacy of a particularly high

4-(2,6-Dichlorophenyl)-4,5-dihydro-3,5-diphenyl-
5,5-(ethylene-1,2-dioxy)-1,2,5-oxazaphosphole-2-oxide

(28°)

Fig. 9 H-nmr



cis and trans

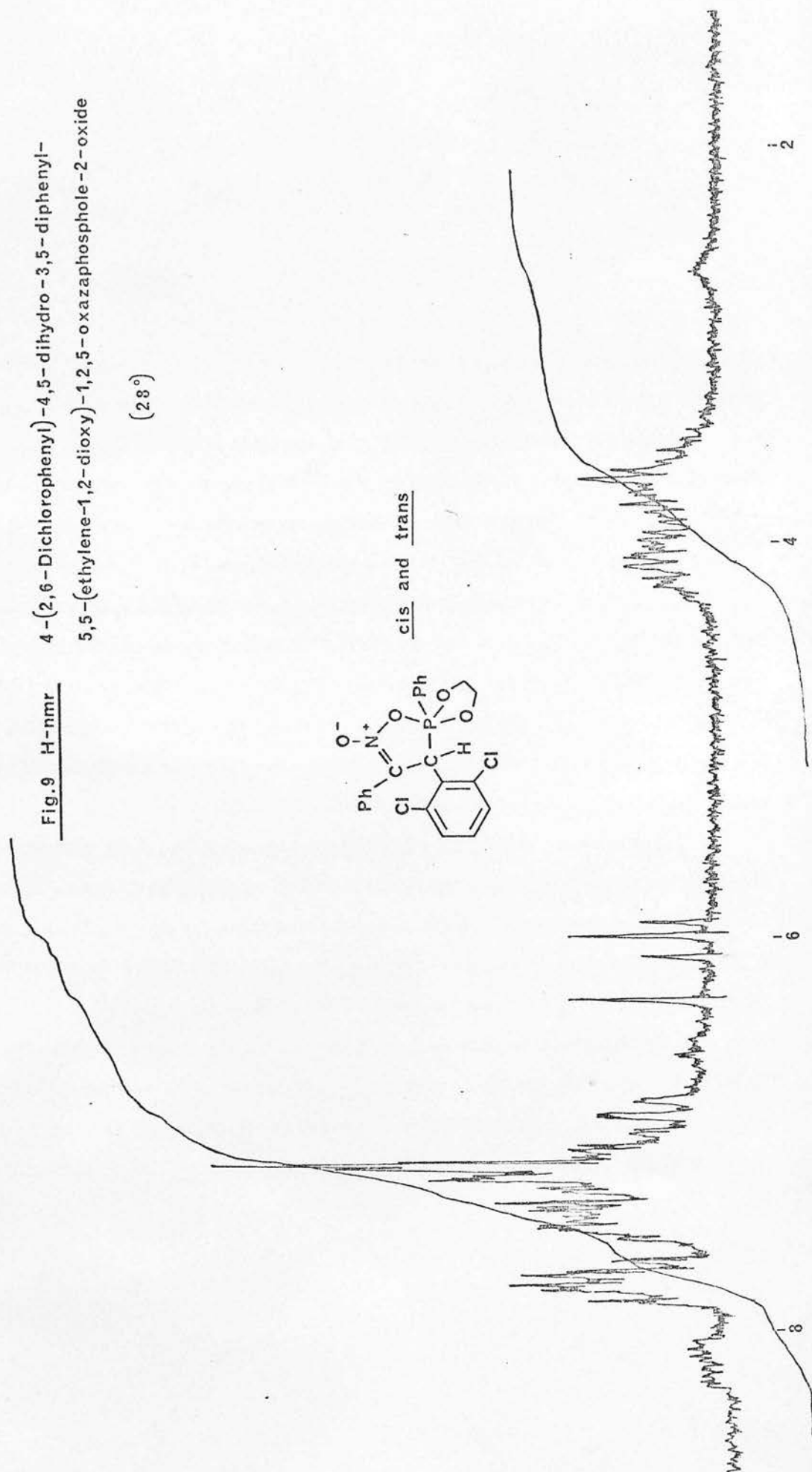
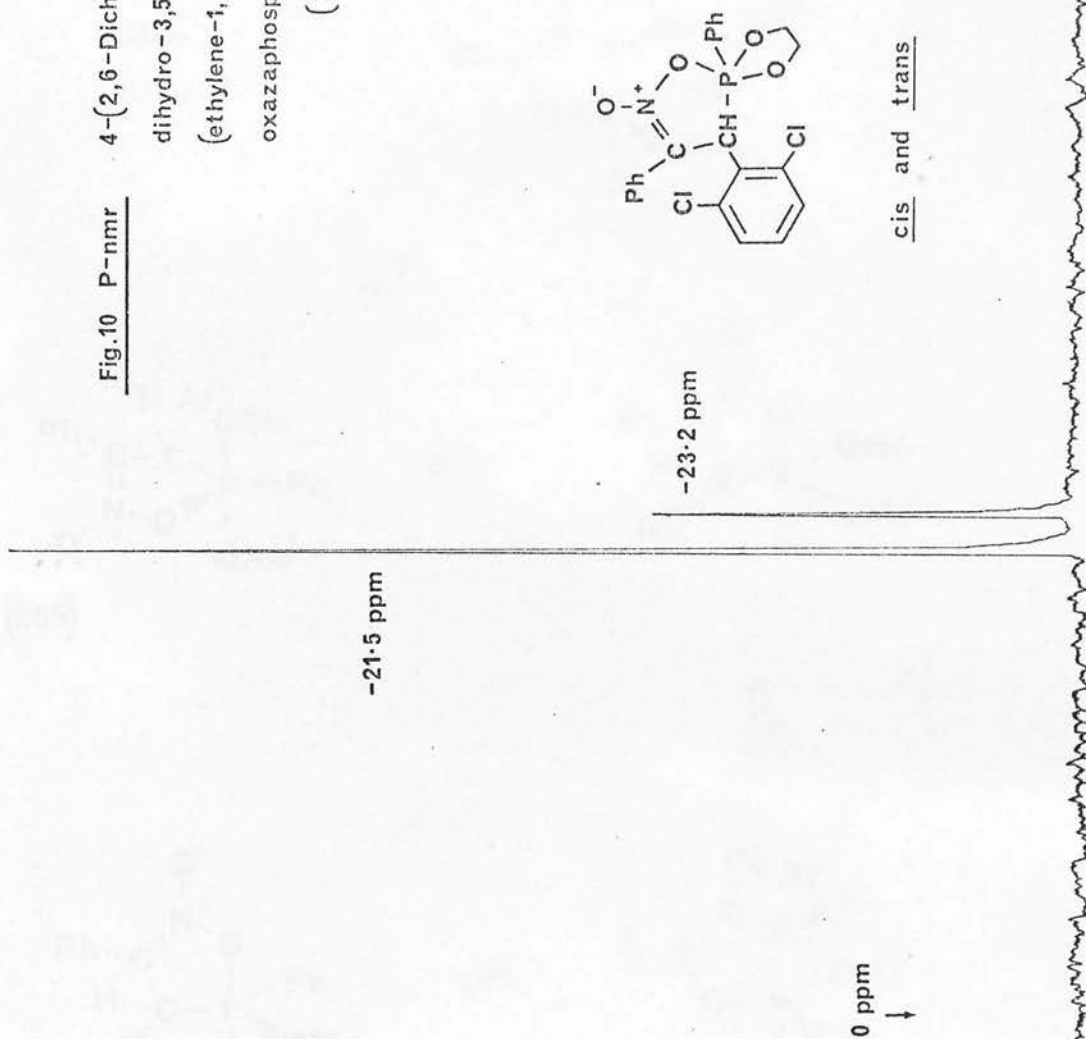
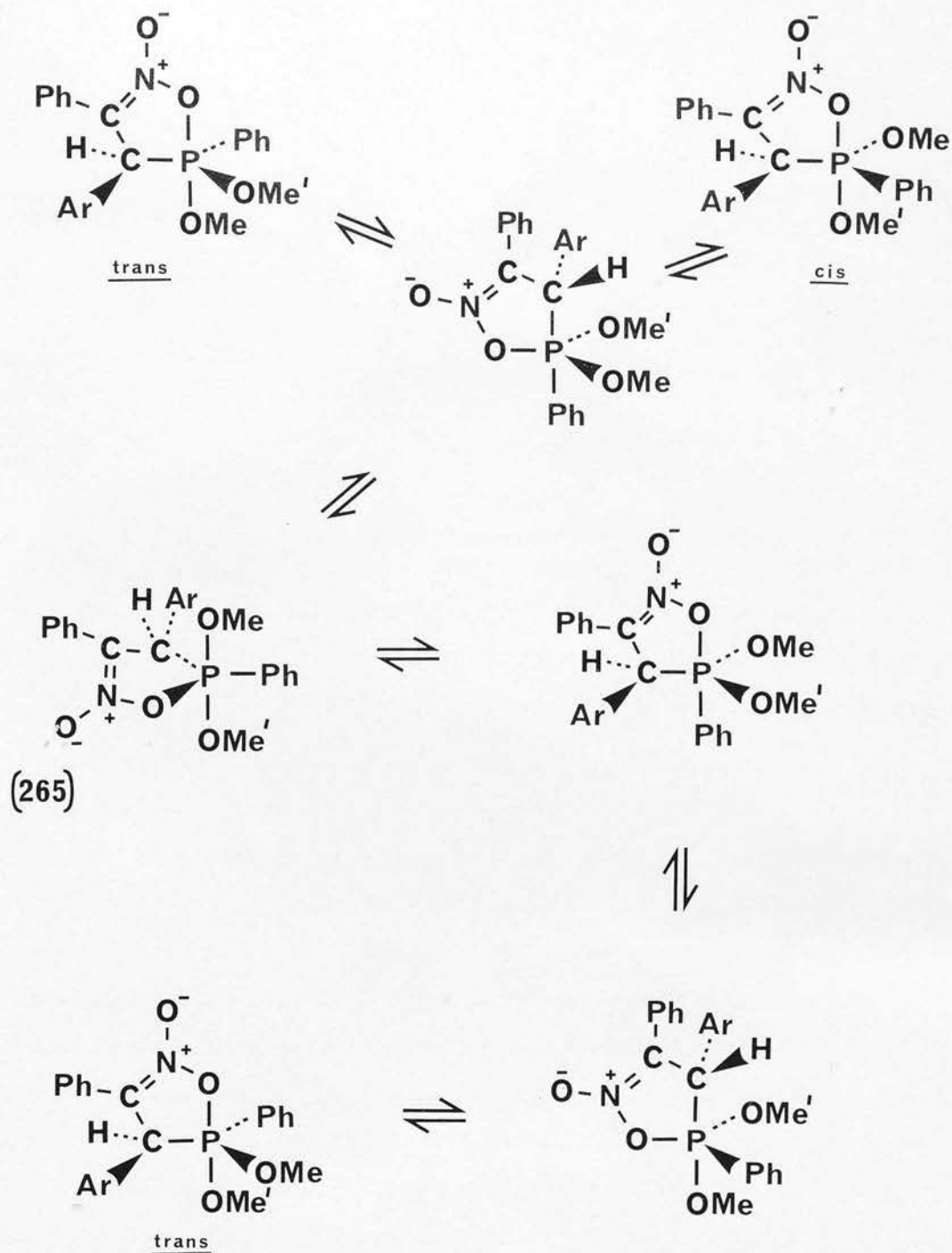


Fig.10 P-nmr 4-(2,6-Dichlorophenyl)-4,5-dihydro-3,5-diphenyl-5,5-(ethylene-1,2-dioxy)-1,2,5-oxazaphosphole-2-oxide
(28°)



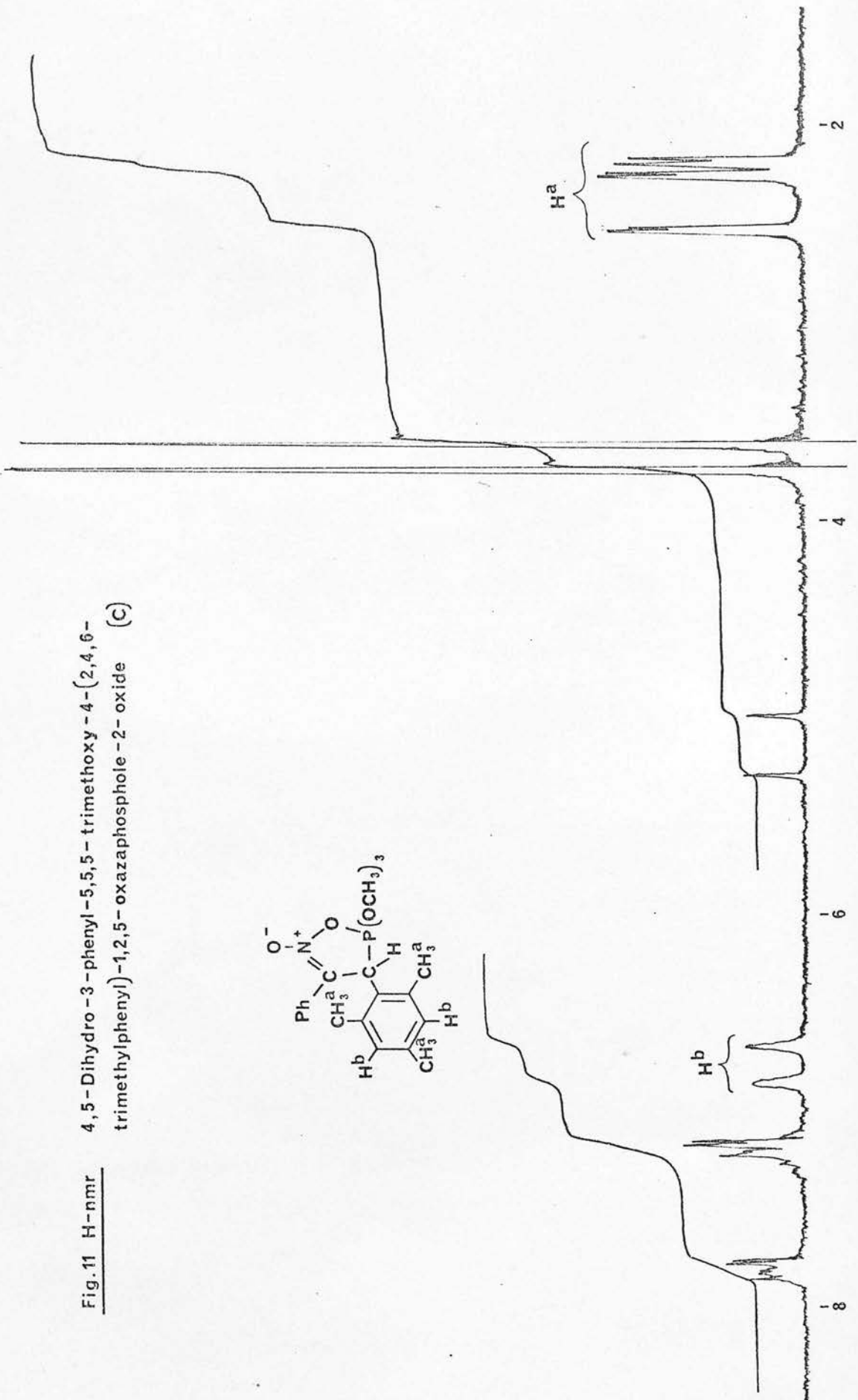
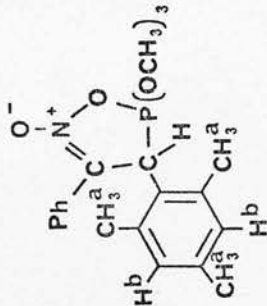


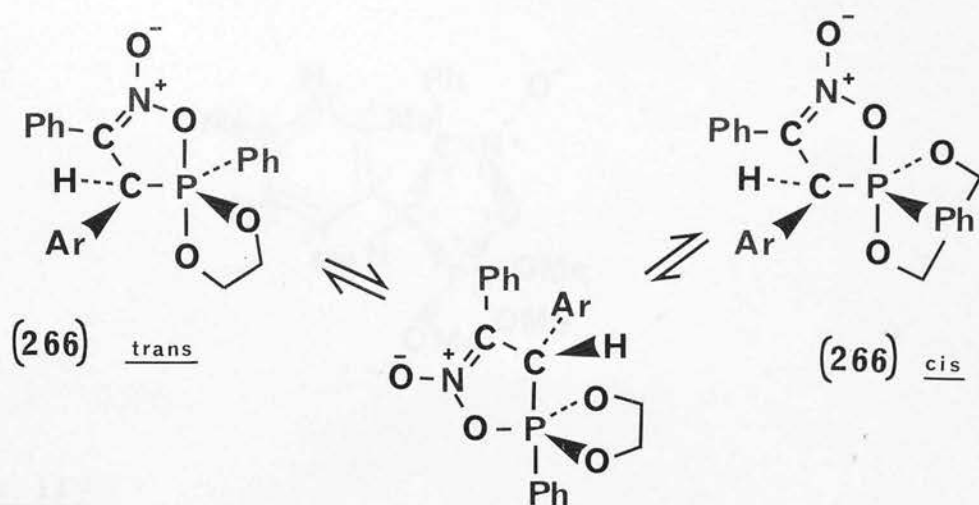
Scheme 158

energy species having a five-membered ring which spans two equatorial sites, which is responsible for hindering the pseudorotation pathway (scheme 159).

Fig. 11 H-nmr

4,5-Dihydro-3-phenyl-5,5,5-trimethoxy-4-(2,4,6-trimethylphenyl)-1,2,5-oxazaphosphole-2-oxide (c)





Scheme 159

Heating a solution of a bicyclic 1,2,5-oxazaphosph(v)ole-2-oxide converts the diastereomeric mixture into the single more thermodynamically stable isomer, which remains pure when the solution is subsequently cooled.

Another line-broadening phenomenon, observed in the cases of 1,2,5-oxazaphosph(v)ole-2-oxides which have a 2,6'-disubstituted 4-aryl group, is indicative of the ring structure and is not connected with the pseudorotation process. The ^1H n.m.r. spectrum of the 1,2,5-oxazaphosph(v)ole-2-oxide, C, (Figure 11) shows three separate methyl signals, each one weakly coupled to the phosphorus nucleus, and two broad signals ascribed to the meta-hydrogens of the 4-aryl group. This suggests that the two ortho-methyl groups and the two meta-hydrogens are not equivalent, which is the case only if rotation of the 4-aryl group about the $\text{C}_{\text{aryl}}-\text{C}_4$ bond is restricted. The size of the ortho-groups apparently constrains the 4-aryl group to a fixed conformation relative to the plane of the phosph(v)ole ring (Figure 12), and in this situation substituents in the 2'- and 3'-positions of the aryl ring are clearly in a different environment from those in the 6'- and 5'-positions. This effect is also observed to a varying degree in compounds D, G, J, K and N (Tables 5 and 6).

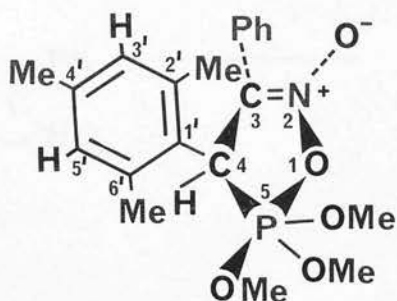
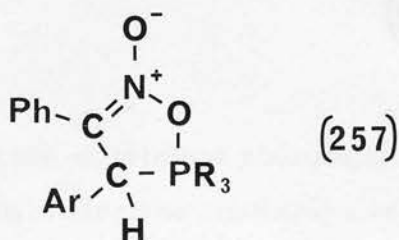


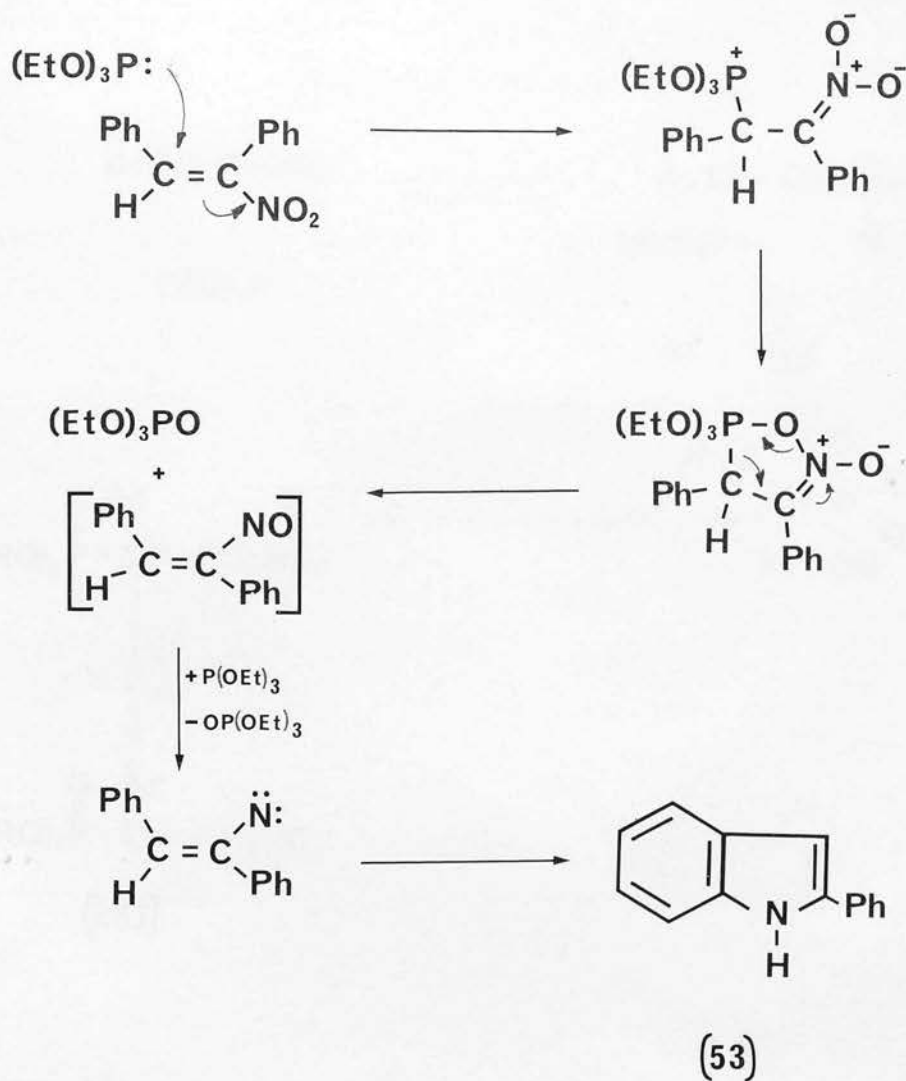
Figure 12

A. 3 The role of 1,2,5-oxazaphosph(v)ole-2-oxide as an intermediate.

The discovery that 4,5-dihydro-3,4-diaryl-1,2,5-oxazaphosph(v)ole-2-oxides (257) were readily prepared by the reactions of 1,2-diaryl-nitroethenes with tervalent phosphorus reagents at room temperature



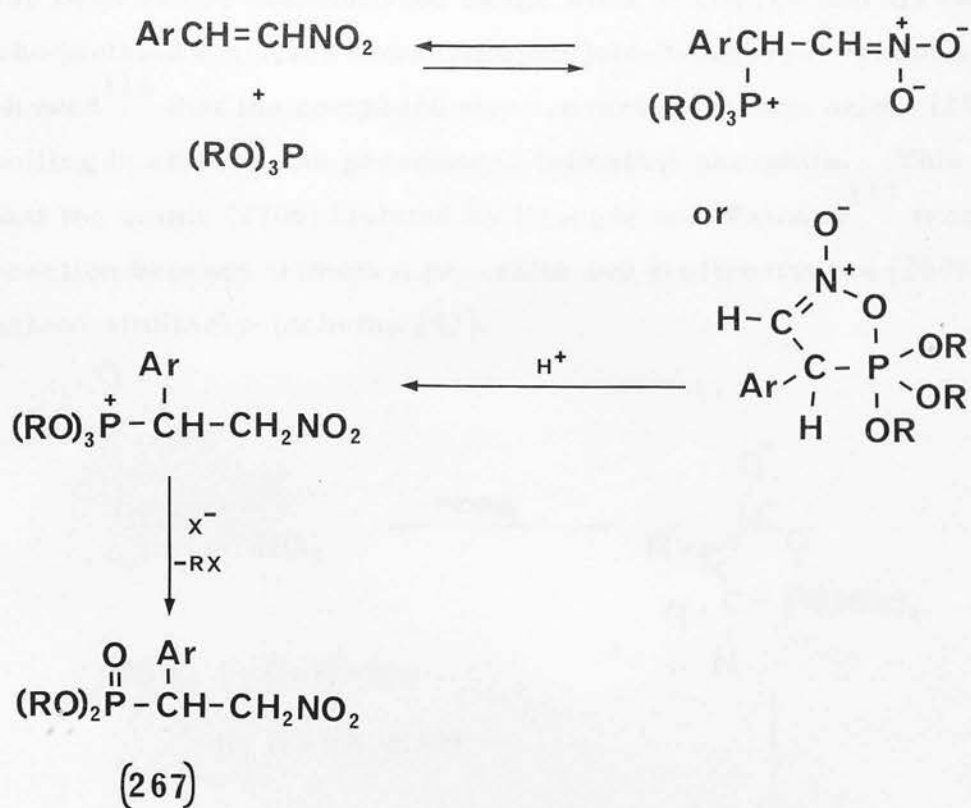
(section A. 2) prompted an investigation into the possibility that the 1,2,5-oxazaphosph(v)ole-2-oxides might be formed under the normal deoxygenation conditions and be intermediates in the formation of nitrene-derived products such as 2-phenylindole. A postulated mechanism (scheme 160) involves the initial formation of 4,5-dihydro-2,3-diphenyl-5,5,5-triethoxy-1,2,5-oxazaphosph(v)ole-2-oxide by Michael-type addition of triethyl phosphite to the activated double bond of 1,2-diphenylnitroethene. The 1,2,5-oxazaphosph(v)ole-2-oxide then



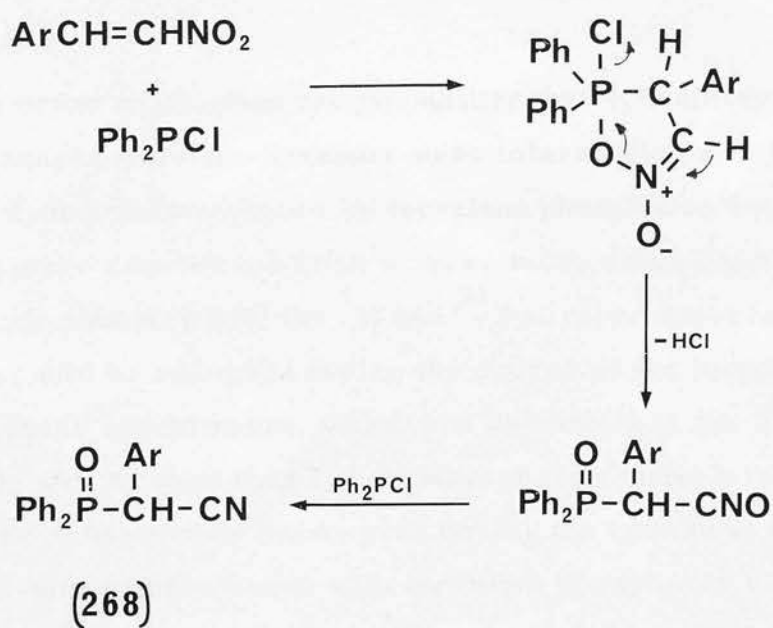
Scheme 160

collapses to give a molecule of triethyl phosphate and a transient nitroso-compound, which, under the conditions of the reaction, would rapidly be deoxygenated to the nitrene, and hence would give 2-phenylindole (53).

In the reaction of trialkyl phosphites with β -nitrostyrenes to give 2-nitroalkylphosphonates (267), Teichmann and his co-workers¹¹⁸ have suggested that a 1,2,5-oxazaphosph(v)ole-2-oxide may be an intermediate (scheme 161). Similarly a $\underline{\text{P}}$ -chloro 1,2,5-oxazaphosph(v)ole-2-oxide has been postulated as an intermediate in the reaction of diphenylphosphinous chloride with β -nitrostyrenes¹¹⁹ to give nitrile-substituted phosphine oxides (268; scheme 162). However, the 1,2,5-oxazaphosph(v)ole-2-oxides postulated by Teichmann have not been isolated or



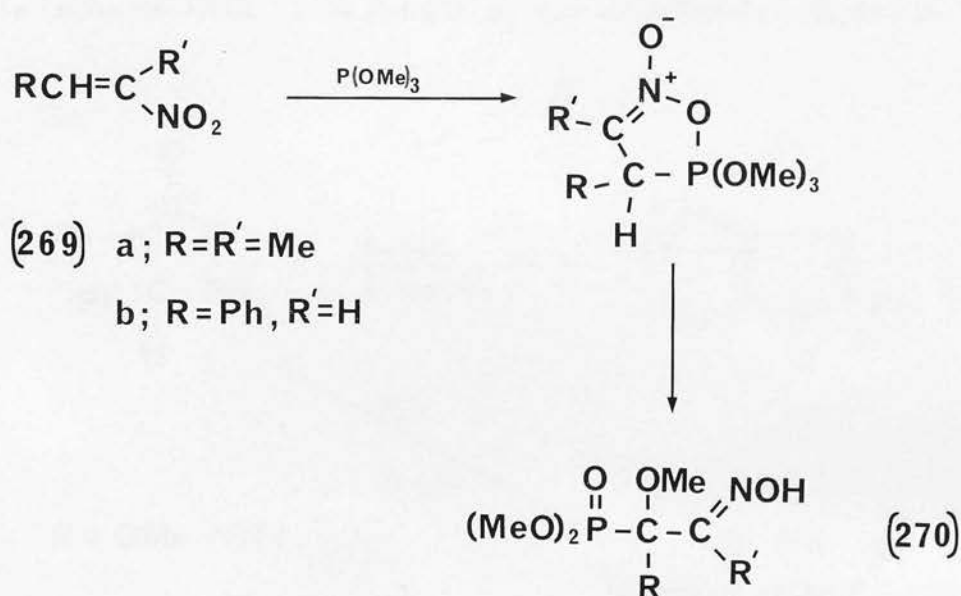
Scheme 161



Scheme 162

detected spectroscopically.

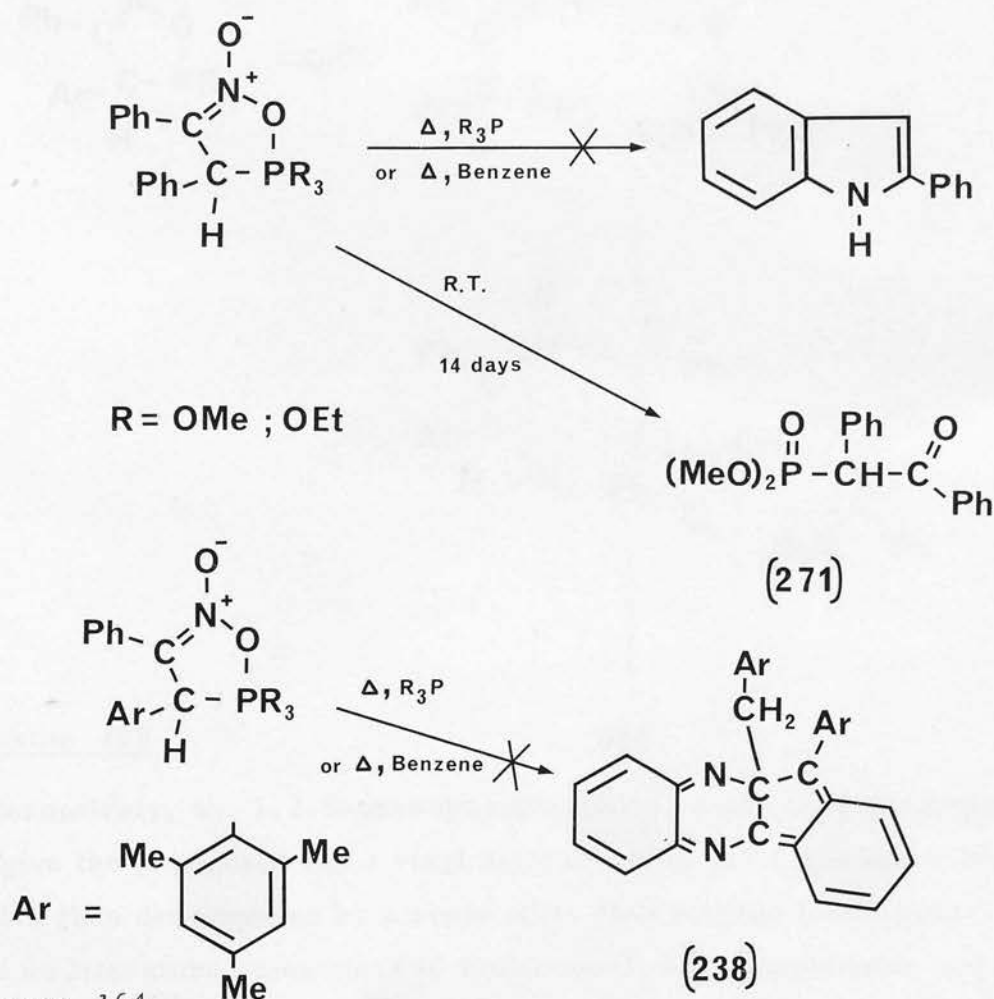
The role of a 1,2,5-oxazaphosph(v)ole-2-oxide as an intermediate has been better substantiated by the work of Gareev and his co-workers,¹¹¹ who isolated the 1,2,5-oxazaphosph(v)ole-2-oxide (269a) and later showed¹¹² that the compound was converted into the oxime (270a) by boiling in ether in the presence of trimethyl phosphite. This suggests that the oxime (270b) isolated by Krueger and Maloney¹¹⁷ from the reaction between trimethyl phosphite and β -nitrostyrene (269b) may have arisen similarly (scheme 163).



Scheme 163

In order to examine the possibility that 4,5-dihydro-2,3-diaryl-1,2,5-oxazaphosph(v)ole-2-oxides were intermediates in the deoxygenation of 1,2-diarylnitroethenes by tervalent phosphorus reagents, the reactions were carried out in an n.m.r. tube, using benzene- d_6 as solvent. In this way both the ^1H and ^{31}P n.m.r. spectra of the reaction mixtures could be recorded during the course of the reaction. The result of these experiments, which are described in the Experimental section D, was to show that 1,2,5-oxazaphosph(v)ole-2-oxides are formed and subsequently decompose during the course of the reactions of the 1,2-diarylnitroethenes with tervalent phosphorus reagents. Less conclusive evidence for the formation of a 1,2,5-oxazaphosph(v)ole-2-oxide was obtained in the case of reaction of β -nitrostyrene with triethyl phosphite.

However, when pure samples of 4,5-dihydro-2,3-diphenyl-5,5,5-trimethoxy-1,2,5-oxazaphosph(v)ole-2-oxide were boiled in trimethyl phosphite, or simply thermolysed in benzene, no identifiable products were obtained. Similarly, reaction of triethyl phosphite with 4,5-dihydro-3,4-diphenyl-5,5,5-triethoxy-1,2,5-oxazaphosph(v)ole-2-oxide failed to give identifiable products. The corresponding thermolyses and reactions with trialkyl phosphites of 4,5-dihydro-3-phenyl-4-(2,4,6-trimethylphenyl)-5,5,5-triethoxy- and 5,5,5-trimethoxy-1,2,5-oxazaphosph(v)ole-2-oxides, which might have been intermediates in the formation of the quinoxaline (238), also failed to give identifiable products (scheme 164). A sample of 4,5-dihydro-2,3-diphenyl-5,5,5-

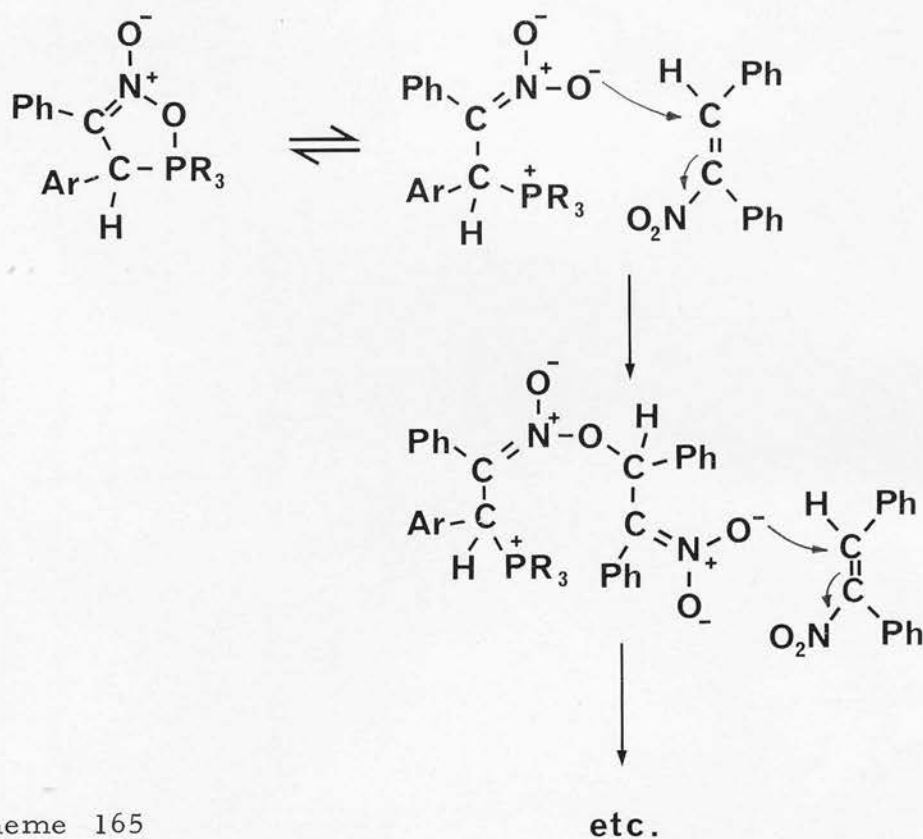


Scheme 164

trimethoxy-1,2,5-oxazaphosph(v)ole-2-oxide decomposed to give a brown oil on standing in a sealed sample bottle at room temperature

for 14 days, and chromatography of the oil afforded dimethyl (1,2-diphenyl)ethan-1-one-2-phosphonate (271).

On the basis of these results alone, the conclusion to be drawn is that 1,2,5-oxazaphosph(v)ole-2-oxides are not intermediates on the route to vinyl nitrenes, the presumed precursors of 2-phenylindole and the quinoxaline (238). Instead, the 1,2,5-oxazaphosph(v)ole-2-oxides appear generally to decompose to give intractable phosphorus-containing materials. Gareev^{115a} has suggested a route to polymeric material which could also apply in this case if the zwitterion into phosph(v)ole conversion is reversible (scheme 165).



Scheme 165

Alternatively, the 1,2,5-oxazaphosph(v)ole-2-oxide may decompose to give the phosphate and a vinyl nitroso-compound (cf scheme 160) which then decomposes by a route other than nitrene formation. There are no literature references to 1-nitroso-1,2-diphenylethene and attempts to prepare it have failed,¹⁸⁶ so the compound is possibly unstable. Either of the above routes which lead to intractable products could also

Fig.13 P-nmr Thermolysis of 4,5-Dihydro-3,4-diphenyl-5,5,5-trimethoxy-1,2,5-oxazaphosphole-2-oxide in C_6D_6 at 78°

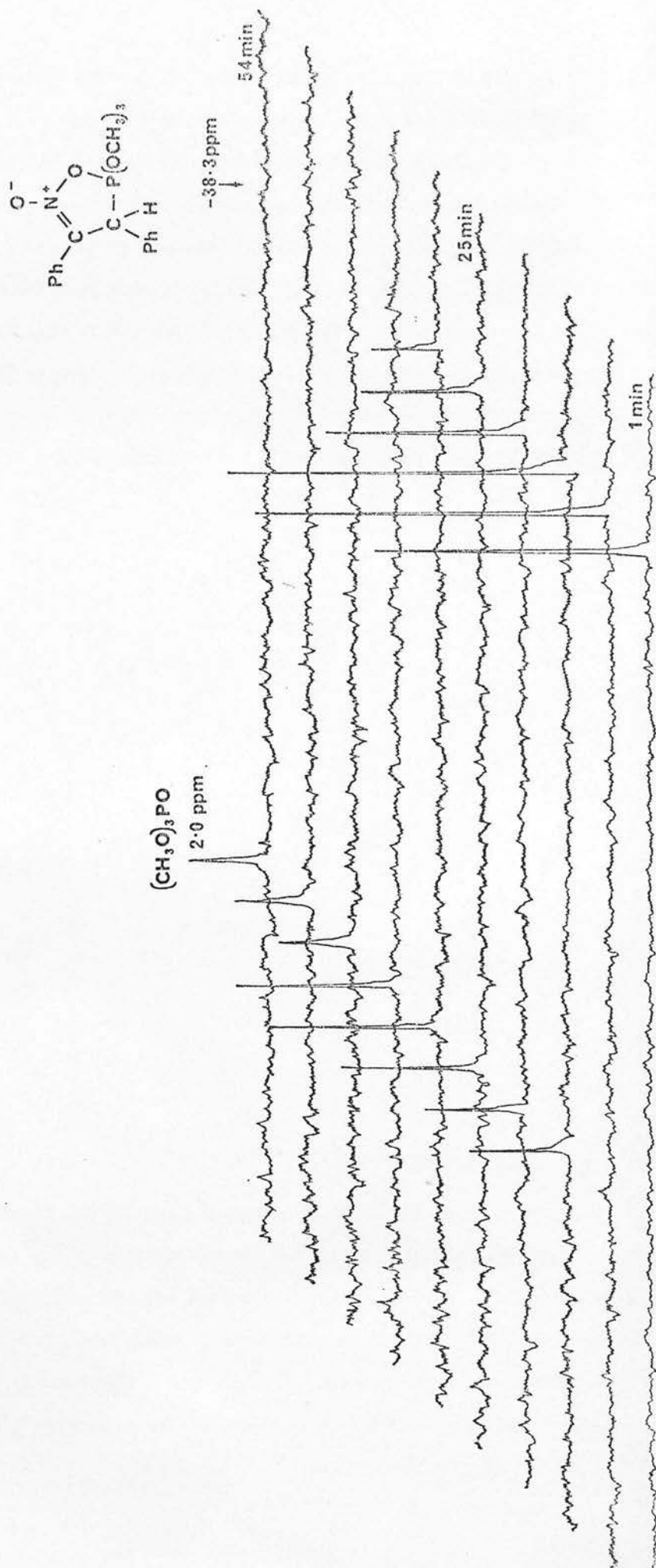
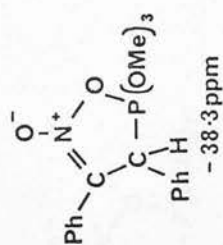


Fig.14 P-nmr

Reaction of 4,5-Dihydro-3,4-diphenyl-5,5,5-trimethoxy-1,2,5-oxazaphosphole-2-oxide with Trimethyl Phosphite at 78°



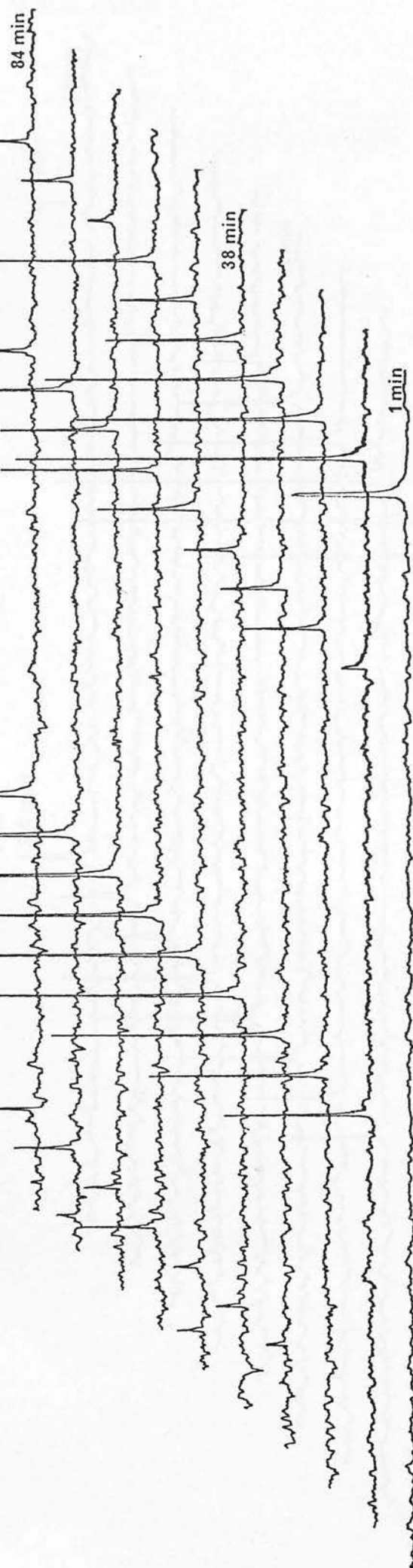
(MeO)₃PO

2.0 ppm

21.3 ppm

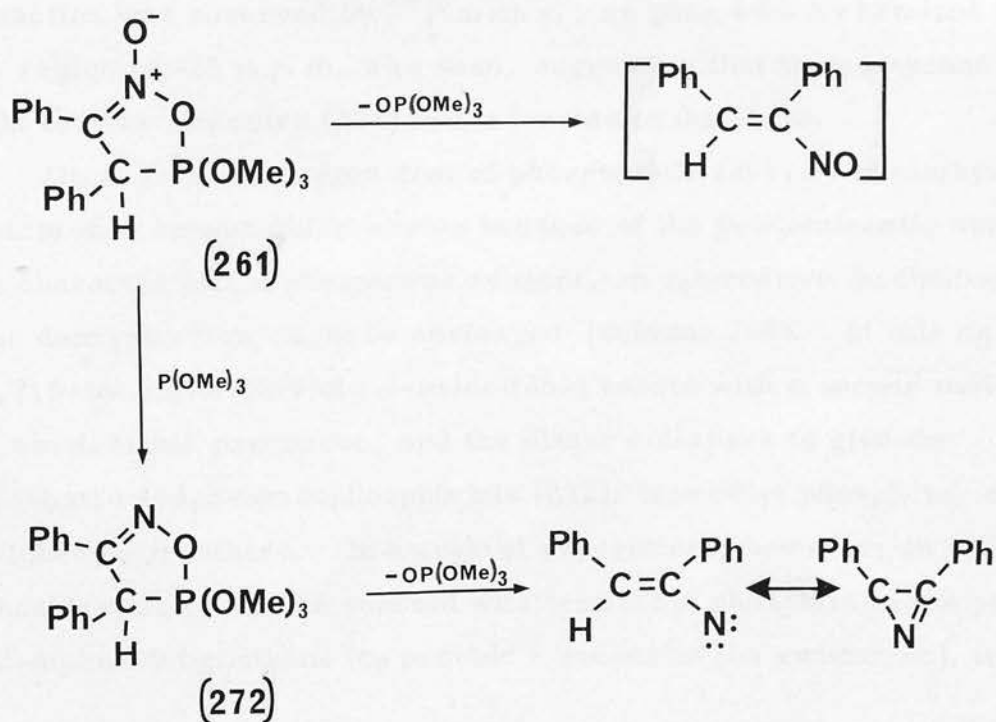
-25.5 ppm

-38.3 ppm



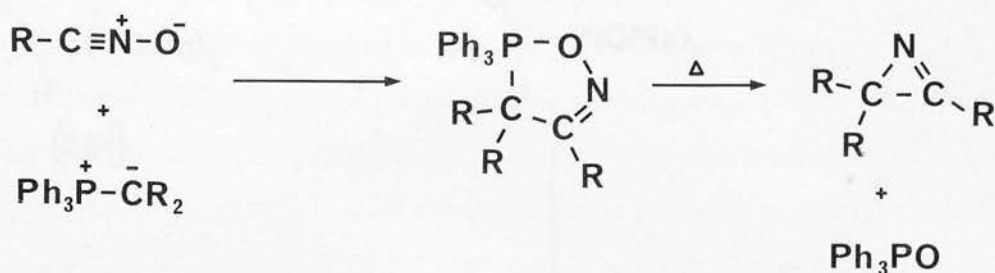
occur under the normal conditions for deoxygenation of the 1,2-diaryl-nitroethenes. However, before dismissing completely the possibility that 1,2,5-oxazaphosph(v)ole-2-oxides are intermediates on the route to vinyl nitrenes, the following observations must be considered.

The thermal decomposition and reaction with trimethyl phosphite of 4,5-dihydro-3,4-diphenyl-5,5,5-trimethoxy-1,2,5-oxazaphosph(v)ole-2-oxide were observed by n. m. r. spectroscopy. The thermal decomposition, as observed by ^{31}P n. m. r. (Figure 13), clearly showed that trimethyl phosphate was the sole phosphorus-containing product, but that in the presence of trimethyl phosphite a more complex reaction occurred (Figure 14). Once again trimethyl phosphate was formed, but an intermediate compound with a ^{31}P shift of -25.5 p. p. m. was also formed. The ^{31}P shift suggests that this may be another pentacoordinate phosph(v)ole (272), and a reasonable suggestion is that the N-oxide function of the initial 1,2,5-oxazaphosph(v)ole-2-oxide has been deoxygenated (scheme 166). Compounds with similar shifts were observed in some of the deoxygenation reactions of 1,2-diarylnitroethenes described in Experimental section D, but no further evidence for the structure of these compounds was obtained.



Scheme 166

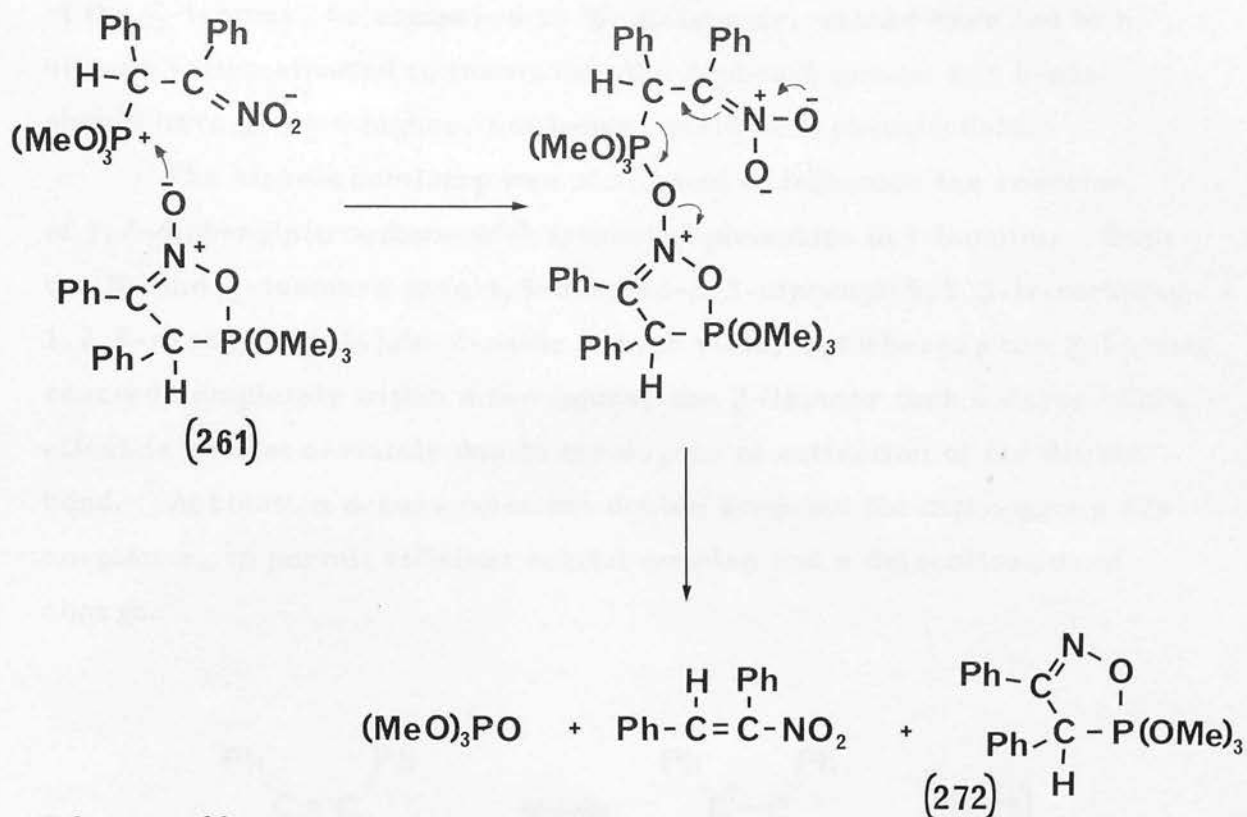
The possibility that a phosph(v)ole (272) is formed during the reaction is significant, because two groups of workers^{98a,c, 105, 106} have shown that analogous 1,2,5-oxazaphosph(v)oles react to give 2H-azirines, a potential source of nitrenes and nitrene-derived products (scheme 167).



Scheme 167

If a nitrene is to be formed via both the intermediates (261) and (272), the most unfavourable step would be the deoxygenation of the N-oxide function of (261) by phosphite. Phosphorus trichloride might be expected to achieve this deoxygenation more readily¹⁰ and give greater yields of nitrene products. However, it was found that reaction of phosphorus trichloride with 4,5-dihydro-2,3-diphenyl-5,5,5-trimethoxy-1,2,5-oxazaphosph(v)ole-2-oxide gave no identifiable products, and when the reaction was observed by ³¹P n. m. r., no peak with a chemical shift in the region of -25 p. p. m. was seen, suggesting that the compound thought to have structure (272) is not formed in this case.

Although the deoxygenation of phosph(v)ole (261) by trimethyl phosphite may appear unfavourable because of the predominantly nucleophilic character of the phosphorus reagent, an alternative mechanism for the deoxygenation might be envisaged (scheme 168). In this case the 1,2,5-oxazaphosph(v)ole-2-oxide (261) reacts with a second molecule of its zwitterionic precursor, and the dimer collapses to give the deoxygenated 1,2,5-oxazaphosph(v)ole (272), trimethyl phosphate, and 1,2-diphenylnitroethene. In a control experiment, however, in which the phosph(v)ole (261) was reacted with trimethyl phosphite in the presence of 1,2-diphenylnitroethene (to provide a source of the zwitterion), no



Scheme 168

improved yield of 2-phenylindole was recorded, thus casting doubt on this proposed mechanism.

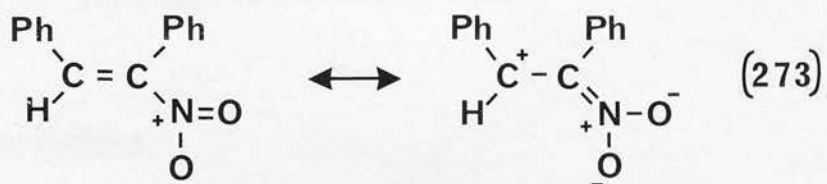
A. 4 Effects of the stereochemistry of the 1,2-diaryl-1-nitroethenes.

The 1,2-diaryl-1-nitroethenes prepared by Robertson's method¹³⁸ for the deoxygenation studies were of the E-configuration, i.e. the phenyl groups were cis. Several groups of workers^{140, 179} have distinguished between the two isomers, E and Z, of 1,2-diphenylnitroethene and comparison of u.v. spectra and the n.m.r. chemical shifts of the 2-hydrogens showed that the substituted nitroethenes were of the E-configuration.

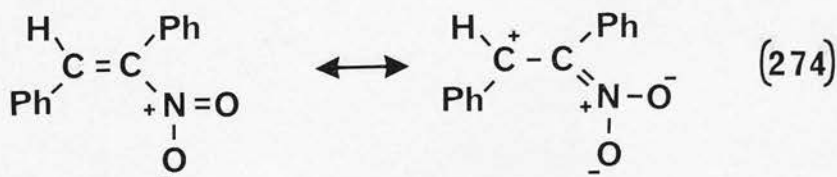
As discussed in section A.1, the E- and Z-isomers of 1,2-diphenylnitroethene both reacted with boiling triethyl phosphite to give 2-phenylindole in 16 and 8% yields respectively. This small variation of yield with stereochemistry was not as expected, because deoxygenation

of the Z-isomer, as compared to the E-isomer, should have led to a nitrene better situated to insert into the 2-phenyl group, and hence should have given a higher, not lower, yield of 2-phenylindole.

The stereochemistry was also found to influence the reaction of 1,2-diphenylnitroethene with trimethyl phosphite in *t*-butanol. Both the E- and Z-isomers gave 4,5-dihydro-2,3-diphenyl-5,5,5-trimethoxy-1,2,5-oxazaphosph(v)ole-2-oxide in high yield, but whereas the E-isomer reacted completely within a few hours, the Z-isomer took 6 days. This effect is almost certainly due to the degree of activation of the double bond. Activation occurs when the double bond and the nitro-group are co-planar, to permit efficient orbital overlap and a delocalisation of charge.



The contribution of canonical form (273) to the structure of the E-isomer is sufficient to ensure that C-2 of the nitroethene is considerably electrophilic. However, in the case of the Z-isomer, the planarity of the molecule is disturbed by the presence of a phenyl group cis to the nitro-group.¹⁴⁰ The contribution of the canonical form (274) is therefore less than that of (273) in the E-isomer and the reduced electrophilicity

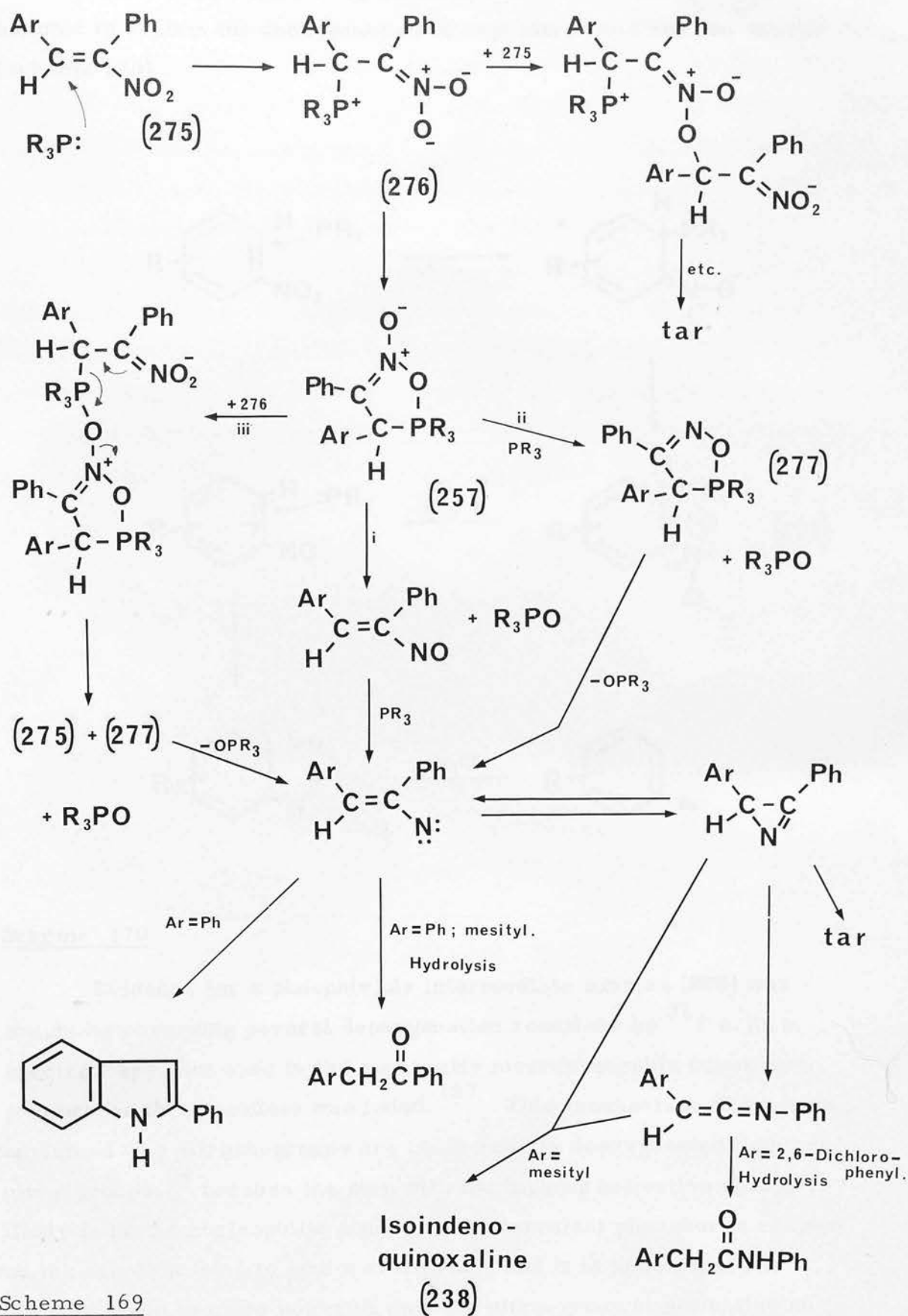


of C-2 slows down the addition of trimethyl phosphite. The lower effective positive charge on C-2 of the Z-isomer is also reflected in the n.m.r. chemical shift of the 2-hydrogen. For the E-isomer this is 8.15 δ , considerably higher in frequency than the usual olefinic range, but the shift of the 2-hydrogen of the Z-isomer (6.80 δ) lies just outside the "normal" olefinic region of the spectrum.

When the reaction of 1,2,2-triphenylnitroethene with trimethyl phosphite was observed by ^{31}P n.m.r. spectroscopy, there was no evidence to support the formation of a 1,2,5-oxazaphosph(v)ole-2-oxide, and no reaction occurred in t-butanol. It is reasonable to assume in this case that the planarity of the molecule is disturbed at least as much as in Z-1,2-diphenylnitroethene, and this, combined with the steric hindrance afforded by an extra phenyl group, effectively stops Michael-type addition of the phosphite to the double bond.

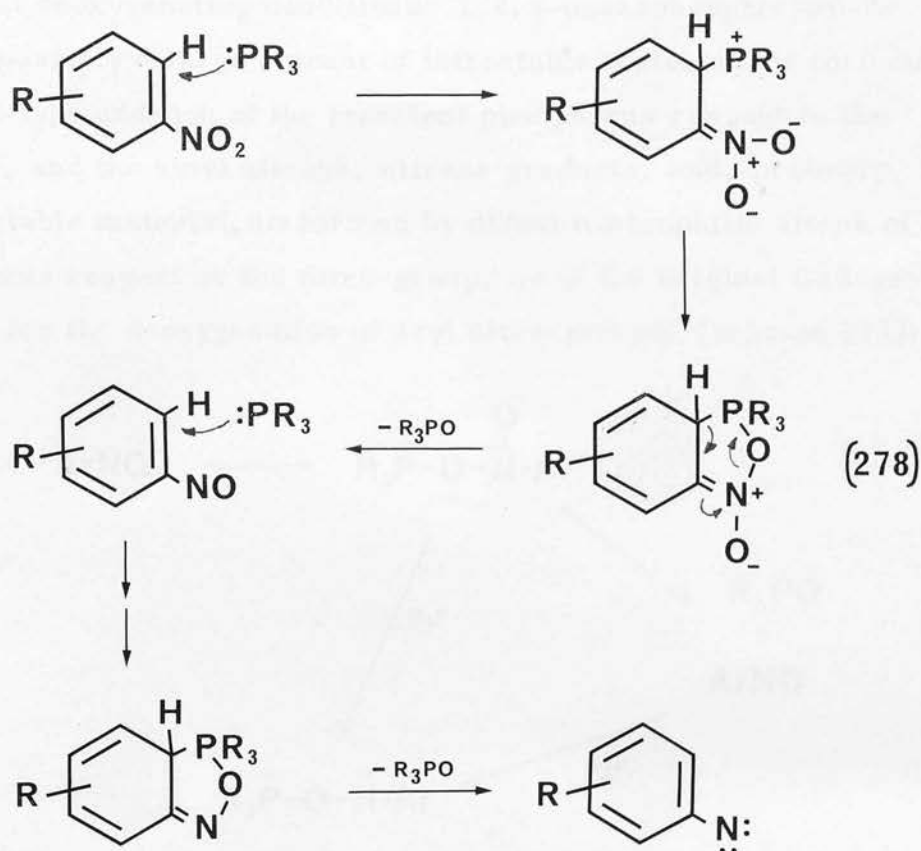
A. 5 Conclusions

During the course of the investigations described above, a mechanism was sought which would provide a unified explanation of the products obtained from the reactions of 1,2-diarylnitroethenes with trivalent phosphorus reagents. From an early stage of the research the formation of 1,2,5-oxazaphosph(v)ole-2-oxides seemed to offer a probable low energy pathway to the vinyl nitrene, hence the observed products, and a mechanism was devised as experimental results became available (scheme 169). Each of the steps in the mechanism has been discussed individually above.



Scheme 169

There was also some speculation that this mechanism could be adapted to explain the deoxygenation of aryl nitro- and nitroso-groups (scheme 170).

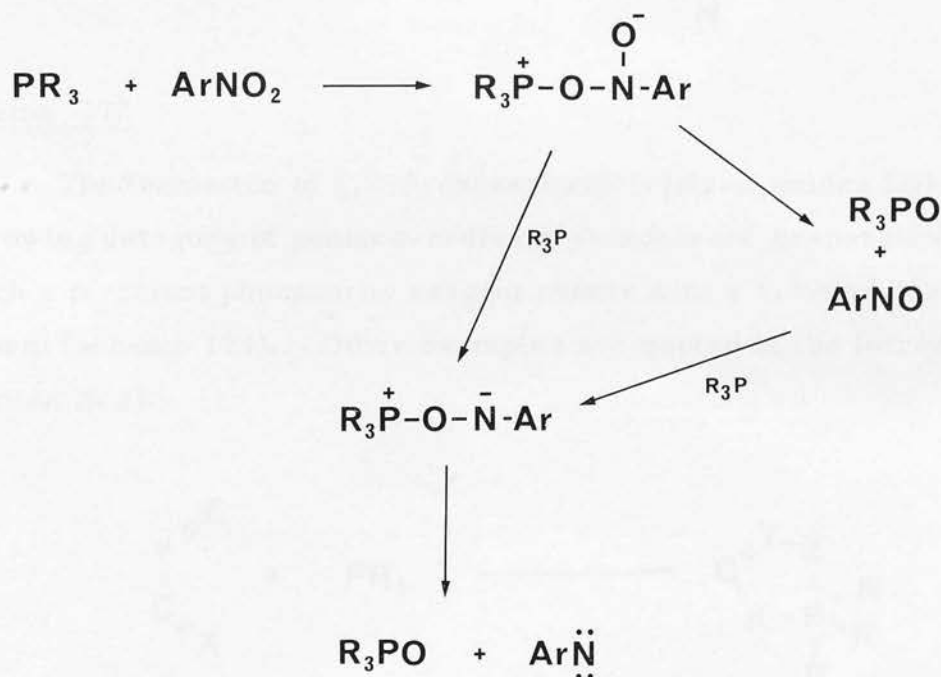


Scheme 170

Evidence for a phosph(v)ole intermediate such as (278) was sought by observing several deoxygenation reactions by ^{31}P n. m. r. spectroscopy, but even in the apparently most favourable cases no support for this postulate was found.¹⁸⁷ This mechanism might have explained why nitroso-groups are more readily deoxygenated than are nitro-groups,³⁴ because the step with the highest activation energy is likely to be the nucleophilic attack by the tervalent phosphorus reagent on the aromatic ring to give a zwitterion, and it is known that the nitroso-group is more powerful than the nitro-group at activating an

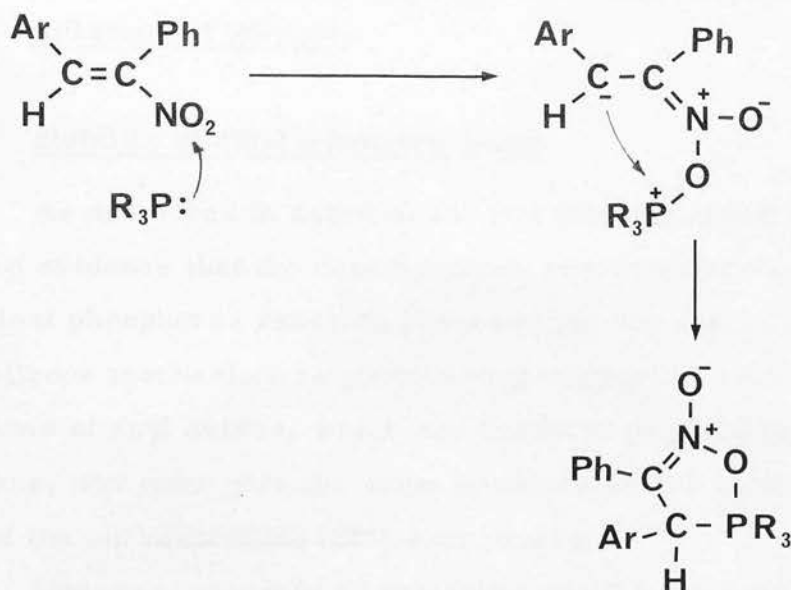
aromatic ring to nucleophilic attack.¹⁸⁸

Attractive as the all-embracing scheme 169 seems to be, the experimental results have failed to show that the 1,2,5-oxazaphosph(v)-ole-2-oxide (257) is an intermediate on the route to nitrene-derived products. The conclusion must be that a dual mechanism is operating under typical deoxygenating conditions: 1,2,5-oxazaphosph(v)ole-2-oxides and possibly a large amount of intractable material are formed via Michael-type addition of the trivalent phosphorus reagent to the double bond, and the vinyl nitrene, nitrene products, and, probably, more intractable material, are formed by direct nucleophilic attack of the phosphorus reagent at the nitro-group, as in the original Cadogan mechanism for the deoxygenation of aryl nitro-groups⁵ (scheme 171).



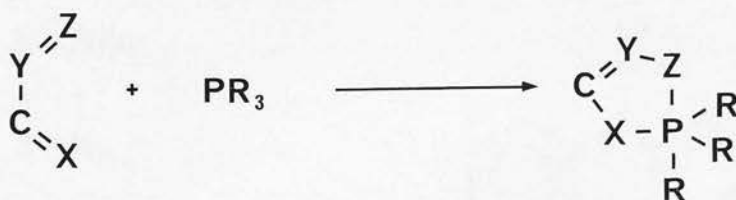
Scheme 171

Formation of the 1,2,5-oxazaphosph(v)ole-2-oxide could conceivably be by initial attack of the phosphorus reagent at the nitro-group (scheme 172), but in view of the polarisation of the $\text{C}=\text{C}-\text{NO}_2$ system, this seems unlikely.



Scheme 172

The formation of 1,2,5-oxazaphosph(v)ole-2-oxides falls into a growing category of pentaco-ordinate phosphorane preparations in which a tervalent phosphorus reagent reacts with a 1,3-unsaturated system (scheme 173). Other examples are quoted in the Introduction (section B. 1).



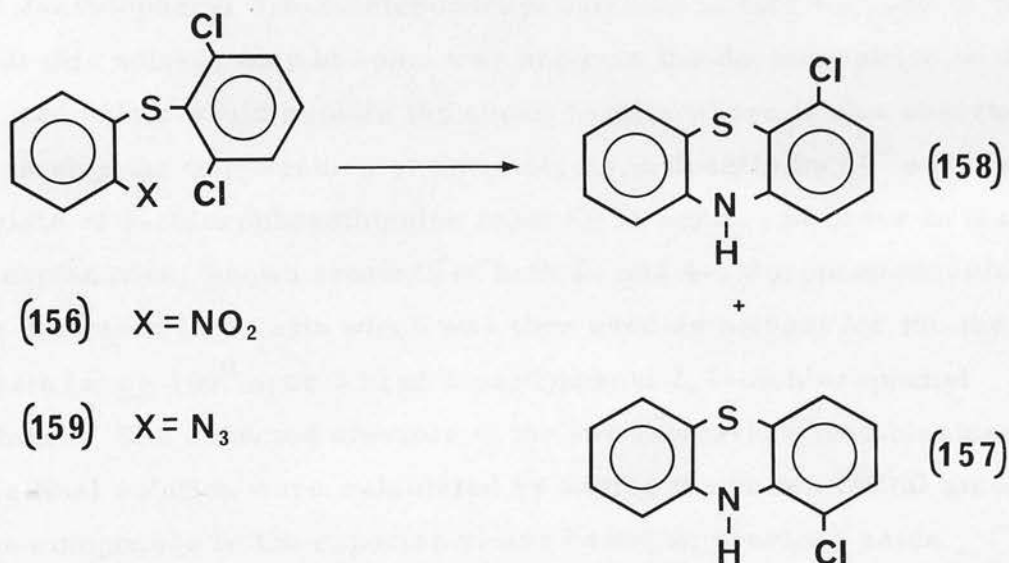
Scheme 173

B. Thermolysis of Aryl 2-Azidophenyl Ethers and Sulphides
and Deoxygenation of the Corresponding Nitro-compounds:-
Influence of Solvents.

B. 1 Stability of chlorophenothiazines

As described in detail in the Introduction (section 3. a), there is good evidence that the deoxygenation of many nitro-compounds by tervalent phosphorus reagents proceeds via nitrene intermediates. The nitrene mechanism is given strong support by studies of the decompositions of aryl azides, which are known to proceed via discrete nitrenes, and often give the same products as are obtained by deoxygenation of the corresponding nitro-compounds.

However, one pair of reactions which gave contrary results was the deoxygenation of 2,6-dichlorophenyl 2-nitrophenyl sulphide and the decomposition of 2-azidophenyl 2,6-dichlorophenyl sulphide (scheme 174).



Scheme 174

The nitro-compound (156), when deoxygenated in neat triethyl phosphite at 152° over a period of 50 h gave 1-chlorophenothiazine (157, 37%) and 4-chlorophenothiazine (158, 52%),⁵¹ whereas thermolysis of the azide (159) in decalin at 150° over 3 h gave the same products, but

in 40% and 5% yields, respectively. Decomposition of the azide (159) in decalin at ca. 190^o, over 2 h, gave only the 1-chloro-isomer (157), in 48% yield. This product variation may be the result of the intermediacy of $\text{Ar}\bar{\text{N}}-\text{O}-\overset{+}{\text{P}}\text{R}_3$ (2) in the nitro/phosphite case, which reacts, without prior decomposition to a nitrene, to give 4-chlorophenothiazine (158) (see schemes 83 and 84).

The result of Holliman's work⁷⁶ in which thermolysis of 2-azidophenyl 2,6-dichlorophenyl sulphide (159) in triethyl phosphate gave the two chlorophenothiazines (157) and (158) in 44% and 23% yield, respectively, may be interpreted as support for this reaction pathway, if one accepts the postulate that the aryl nitrene from thermolysis of the azide (159) can react with phosphate to form the zwitterion (2; see scheme 79). However, the use of triethyl phosphate instead of decalin as solvent for the decomposition of several other 2-azidophenyl aryl sulphides and sulphones failed to produce any significant variations in products.^{50d, 57}

An alternative explanation for the low yield of 4-chlorophenothiazine when 2-azidophenyl 2,6-dichlorophenyl sulphide is thermolysed in decalin is that this solvent may in some way promote the decomposition of the product. This would explain the above results where it was observed that raising the temperature of thermolysis in decalin by 40^o reduced the yield of 4-chlorophenothiazine from 5% to zero. In order to test this explanation, known amounts of both 1- and 4-chlorophenothiazine were dissolved in decalin which was then used as solvent for the thermolysis (at ca 190^o over 2 h) of 2-azidophenyl 2,6-dichlorophenyl sulphide. The expected amounts of the two isomeric phenothiazines in the final solution were calculated by adding the known initial amounts of the compounds to the expected yields based on previous azide thermolyses,⁵¹ and the results were compared with the measured amounts of the two compounds (Table 11).

Table 11

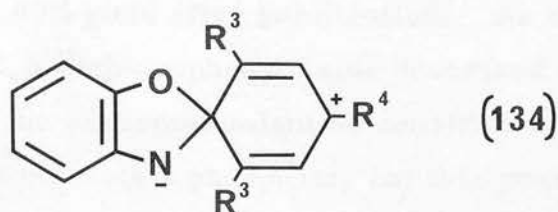
Thermal Stability of Chlorophenothiazines in Decalin

| | Initially | Expected Yield | Expected Total | Actual Total |
|----------------------------|-----------|----------------|----------------|--------------|
| 1-Chlorophenothi- azine | 0.016 g | 0.018 g | 0.034 g | 0.0089 g |
| 4-Chlorophenothi- azine | 0.012 g | 0 | 0.012 g | 0.0046 g |

On the basis of these results it would appear that under the reaction conditions neither isomer is stable to prolonged heating in decalin, but unfortunately this does not explain the variation in yields which occurs under different conditions, as discussed above. Indeed whereas the earlier results suggested that the 4-chloro-isomer might be thermally unstable in decalin, it is the 1-chloro-isomer which in the control experiment has undergone the greater decomposition. The measured amount of 1-chlorophenothiazine is lower than that expected from the thermolysis of the azide alone, determined in previous experiments. This may be an experimental error caused by the small scale of the reaction or, possibly, an indication that the decomposition is accelerated by the presence of decomposition products.

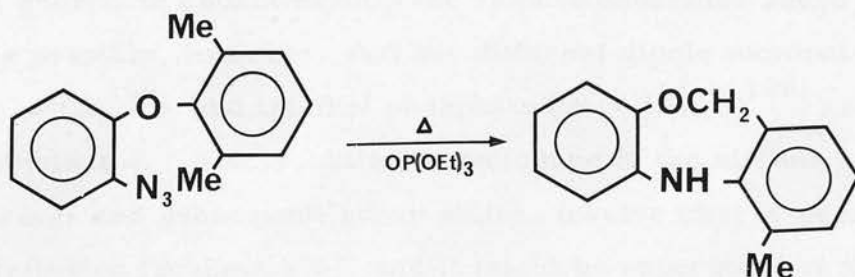
B. 2 Thermolysis of aryl 2-azidophenyl ethers

When certain 2-nitrophenyl aryl ethers react with phosphites, 1,3,2-benzoxazaphosph(v)oles are major products, as described in the Introduction (sections A. 2. e and B. 2). The trivalent phosphorus reagent readily intercepts the postulated spiro-intermediate (134), with the result that yields of non-phosphorus-containing heterocycles are very small, and have been observed in only three cases^{58a} viz. 2,6-dimethylphenyl-, 2,4,6-trimethylphenyl-, and 2,6-dimethoxyphenyl



2-nitrophenyl ethers give, respectively, 5,11-dihydro-4-methyldibenzo- $[b,e][1,4]$ oxazepine (3%), 5,11-dihydro-2,4-dimethyldibenzo $[b,e][1,4]$ -oxazepine (1.5%), and a mixture of 1,2-dimethoxyphenoxazine (2%) and either 1- or 4-methoxyphenoxazine (5%). The decomposition of the analogous azides⁷⁵ gave the same four compounds, but in higher yields, *i. e.* 11, 15, 15, and 35% respectively.

If the attack by phosphite on the spiro-intermediate (134) could be averted, it is possible that good yields of non-phosphorus-containing heterocycles might be formed via the dipolar intermediate (2), $\text{Ar}\bar{\text{N}}-\text{O}-\overset{+}{\text{P}}\text{R}_3$. Although this is not possible under the conditions of a deoxygenation reaction, it can be simulated (if Holliman's suggestion,⁷⁶ that (2) can be formed by reaction of an aryl nitrene with triethyl phosphate, is correct) by decomposing the corresponding aryl azide in triethyl phosphate $[\text{ArN}:\text{ + OP(OEt)}_3 \rightarrow \text{Ar}\bar{\text{N}}-\text{O}-\overset{+}{\text{P}}(\text{OEt})_3 \text{ (2)}]$. It has been noted⁸² that decomposition of 2-azidophenyl 2,6-dimethylphenyl ether in triethyl phosphate gives 5,11-dihydro-4-methyldibenzo $[b,e][1,4]$ -oxazepine (279) in a crude yield of 73% (scheme 175). A repetition of this

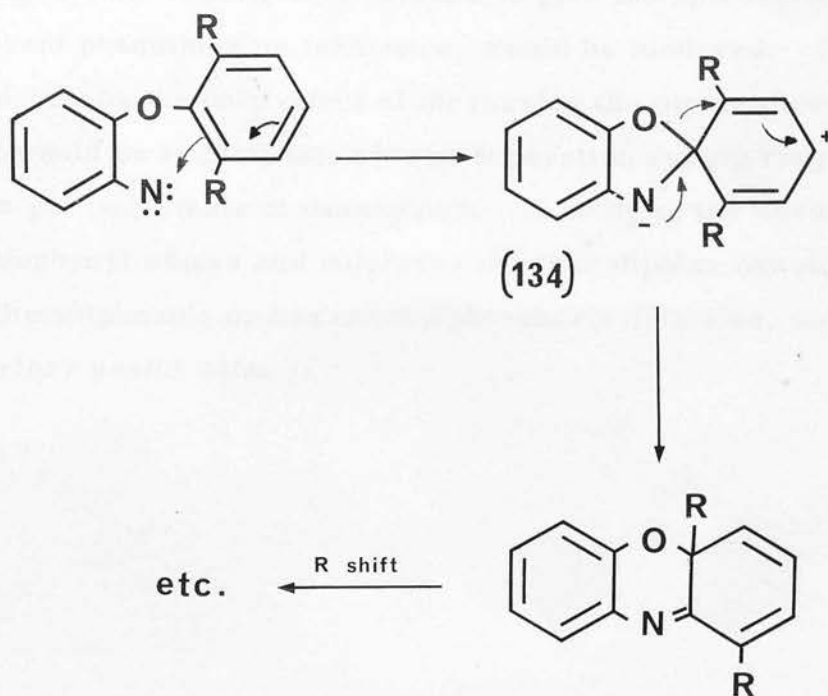


(279)

reaction, described in the Experimental section (F. 1) gave the compound (279) in 48% yield after purification. As with the thermolysis of 2-azidophenyl 2,6-dichlorophenyl azide described above, there was the suspicion that the oxazepine might be sensitive to prolonged heating in decalin, but not in triethyl phosphate, but this possibility has been ruled out by control experiments.

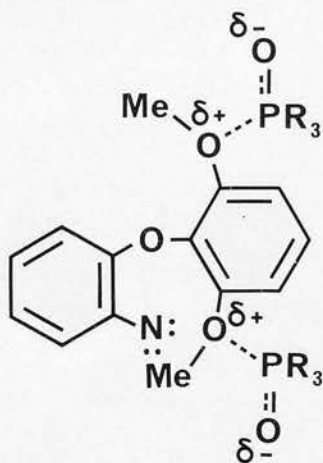
Further experiments (section F. 1) have shown that: (a) decomposition of 2-azidophenyl 2,4,6-trimethylphenyl ether in triethyl phosphate gives 5,11-dihydro-2,4-dimethyldibenzo[b,e][1,4]oxazepine (51%), compared to 15% in decalin;⁷⁵ (b) 1,2-dimethoxyphenoxazine (1.1%) and 4- (or 1-)methoxyphenoxazine (16%), from the decomposition of 2-azidophenyl 2,6-dimethoxyphenyl ether in triethyl phosphate, are obtained in considerably reduced yields, compared with the corresponding reaction in decalin which gives yields of 15 and 35% respectively; (c) thermolysis of 2-azidophenyl 2,6-dichlorophenyl ether in either triethyl phosphate or decalin fails to give identifiable products.

Again, therefore, the use of triethyl phosphate as solvent is found to have a profound effect on certain azide decompositions. In the example discussed previously, the thermolysis of 2-azidophenyl 2,6-dichlorophenyl sulphide (Introduction, section A. 3. a), it was suggested that the zwitterion, $\text{Ar}\ddot{\text{N}}-\text{O}-\overset{+}{\text{P}}(\text{OEt})_3$ (2), formed in triethyl phosphate, could react by a route which did not involve a nitrene (see scheme 84). This is a possible explanation for the variation in products, with solvent, observed in this case, but the formation and reaction of analogous zwitterionic intermediates when 2-azidophenyl 2,4,6-trimethylphenyl ether and 2-azidophenyl 2,6-dimethoxyphenyl ether decompose in triethyl phosphate cannot explain the results described above [(a) and (b)]. It is possible, however, that the different dipole moments of decalin ($\mu = 0\text{D}^{189}$) and triethyl phosphate ($\mu = 3.12\text{D}^{190}$) are a contributory factor. Electrophilic ring closure of the nitrene onto the aromatic ring, and subsequent group shifts, involve charge separation and redistribution (scheme 176), and it might be expected that this would be affected considerably by the polarity of the solvent.



Scheme 176

It is noteworthy that the yields of oxazepines are increased by the use of triethyl phosphate as solvent, whereas the yields of methoxyphenoxazines are decreased. A possible explanation of this effect is that the oxygen atoms of the methoxy-groups offer lone electron pairs for coordination with the polar solvent. This would increase the

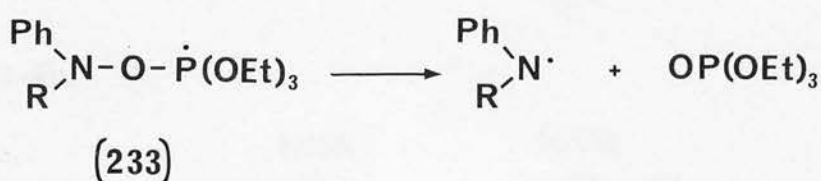


effective size of the group, and decrease the electron density in the benzene ring. As a result, ring closure to give the spiro-dienone (134), and subsequent phenothiazine formation, would be hindered. In the case of o-methyl groups the only effect of increasing the dipole moment of the solvent would be to facilitate charge separation during ring closure, resulting in greater yields of oxazepines. A study of the decomposition of aryl azidophenyl ethers and sulphides in other dipolar aprotic solvents, e. g. dimethylsulphoxide or hexamethylphosphoric triamide, might produce further useful data.

C. Deoxygenation of Nitroxyl Radicals by Tervalent Phosphorus Reagents.

C. 1 Deoxygenation in the presence of competitive nucleophiles

The studies by Cadogan and Rowley¹²⁹ of the deoxygenation of diphenylnitroxyl and N-t-butylphenylnitroxyl radicals by tervalent phosphorus reagents have been described in detail in the Introduction (section C. 2). These reactions were found to give aminyl radicals by β -scission of an intermediate phosphoranyl radical (233, scheme 177;



Scheme 177

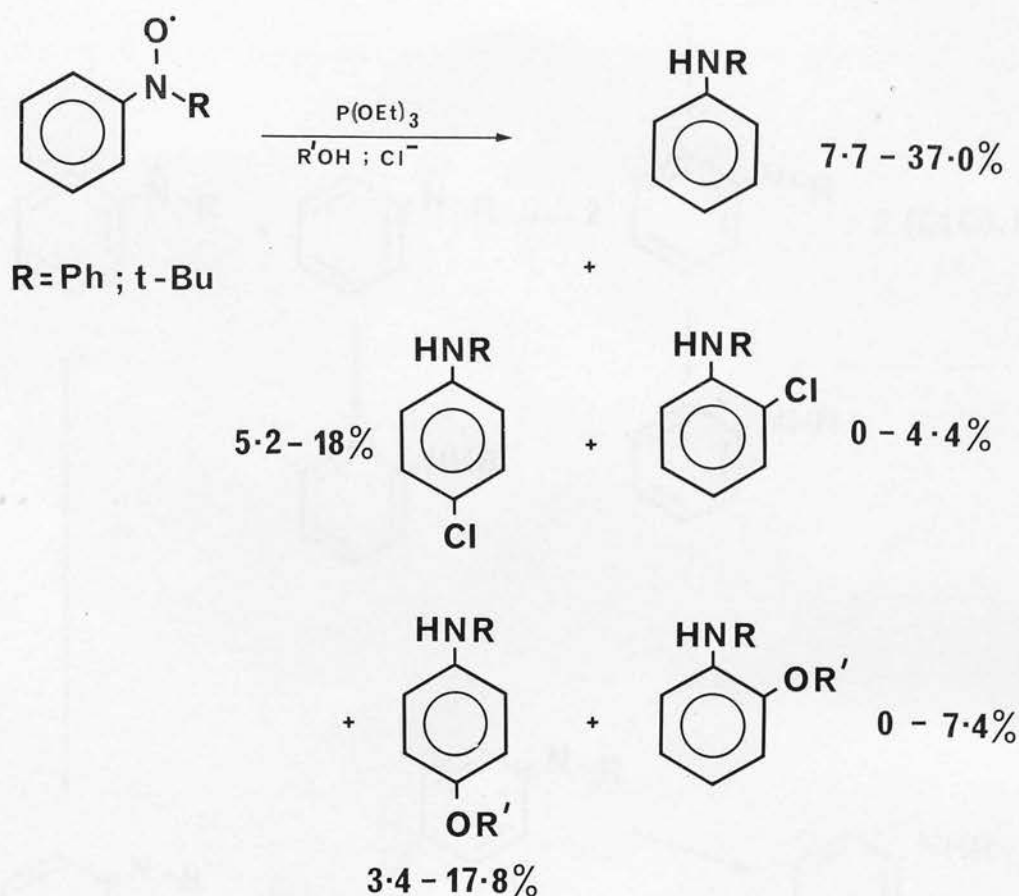
see also scheme 138). This aspect of the mechanism was confirmed by the work of Ang,¹³⁶ and Nigumi and Emeleus.¹³⁵

It was shown that thermolysis of tetraphenylhydrazine, an authentic source of diphenylaminyl radicals,¹³⁰ gave the same results as deoxygenation of diphenylnitroxyl. When the reactions were carried out in benzene the aminyl radical underwent disproportionation to give an aniline and tar, but products arising by substitution at the aromatic nucleus were obtained when the reactions were carried out in methanol or ethanol. Cadogan and Rowley proposed a mechanism which involved electron transfer between aminyl radicals, leading to a delocalised nitrenium ion which could undergo nucleophilic substitution by the solvent (see scheme 140). Although good evidence for the formation of a nitrenium ion was presented, it was decided to seek further proof by attempting similar deoxygenations in the presence of an additional nucleophile, chloride ion.

The deoxygenations of N-t-butylphenylnitroxyl and diphenylnitroxyl by triethyl phosphite were carried out in methanol or ethanol saturated with lithium chloride. The procedure is described in the

Experimental section (G), and a tabulated version of the results is presented.

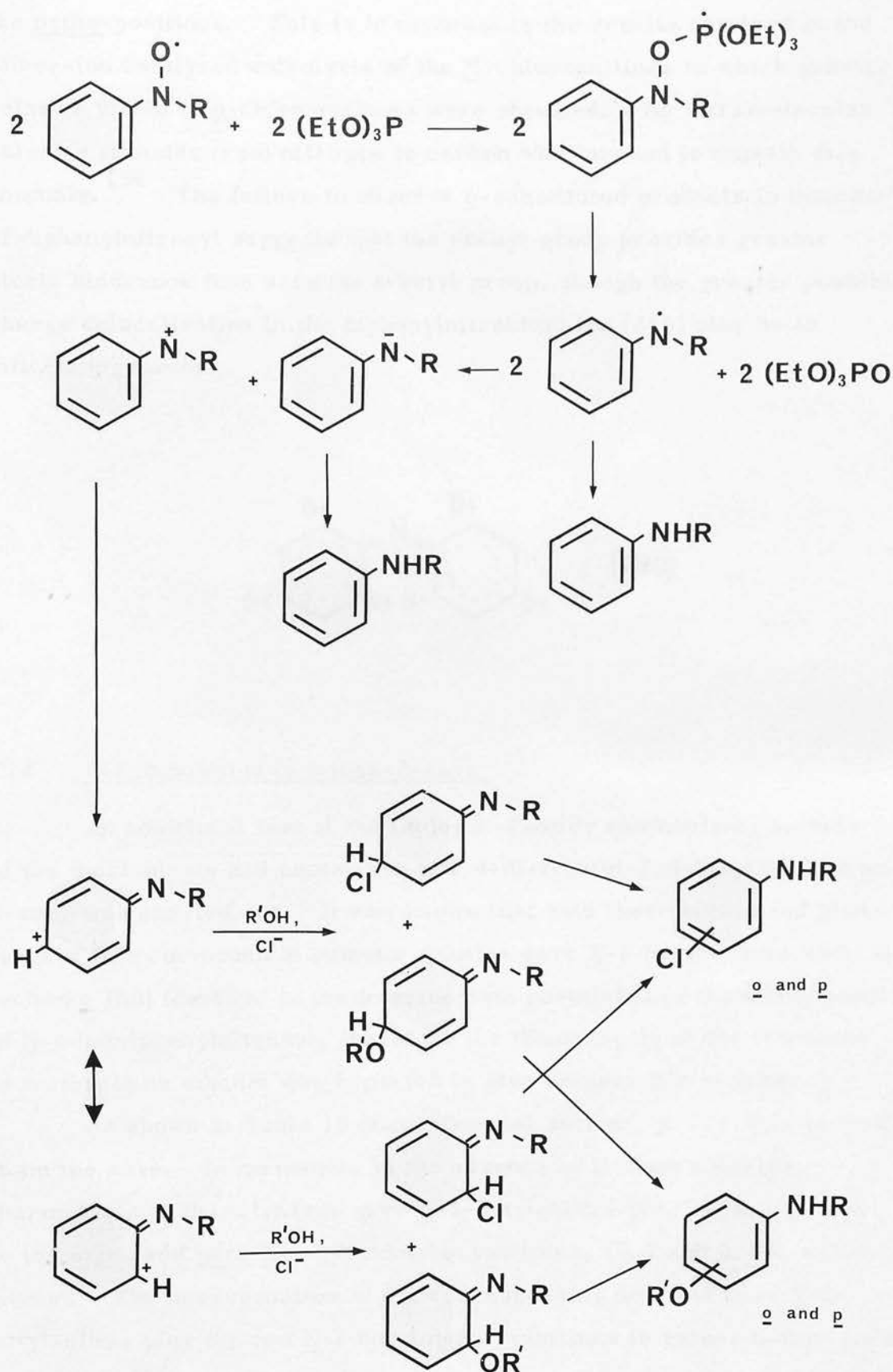
The important result to come out of this investigation is that ring-chlorinated anilines are indeed formed from diphenylnitroxyl and N-*t*-butylphenylnitroxyl under these conditions (scheme 178). For



Scheme 178

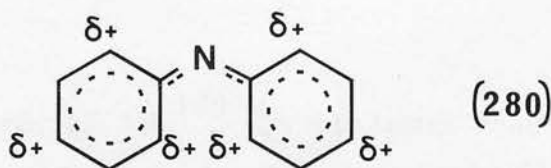
example, deoxygenation of diphenylnitroxyl in ethanol saturated with lithium chloride gives 4-chlorodiphenylamine (6.5%) and deoxygenation of N-*t*-butylphenylnitroxyl in methanol saturated with lithium chloride gives N-*t*-butyl-o-chloroaniline (0.9%) and N-*t*-butyl-p-chloroaniline (5.2%). These last two compounds are obtained in 4.4 and 18.0% yields, respectively, when ethanol is substituted for methanol. The substitution of chlorine in the aromatic nucleus and the pattern of substitution, which is typical of an ionic process, are powerful evidence for the intermediacy

of a delocalised nitrenium ion, lending further support to the mechanism of Cadogan and Rowley (scheme 179).



Scheme 179

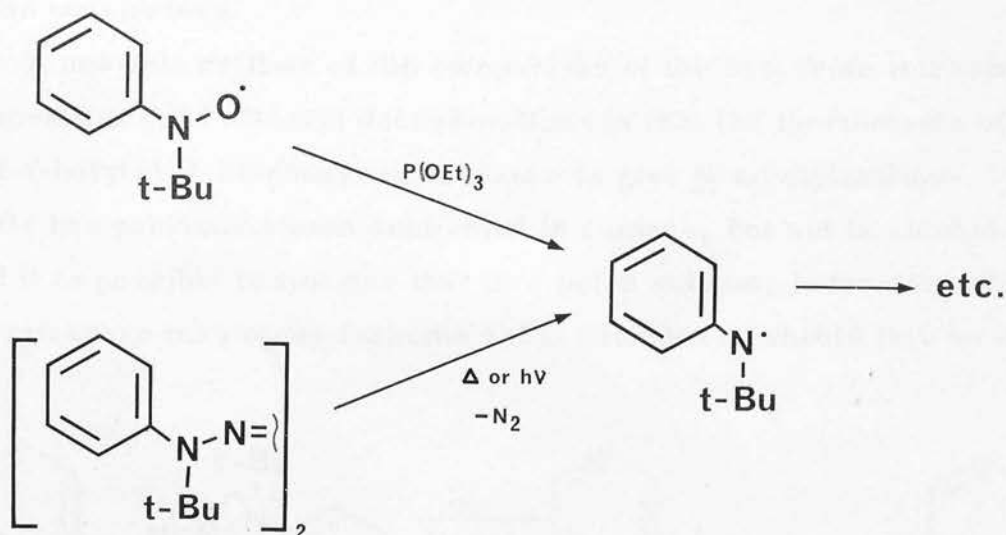
The yields of the p-substituted products are greater than those of the o-substituted products because of steric hindrance to attack at the ortho-positions. This is in contrast to the results obtained in the silver-ion catalysed solvolysis of the N-chloroanilines in which greater relative yields of o-chloroanilines were obtained. An intramolecular chlorine transfer from nitrogen to carbon was invoked to explain this anomaly.¹³⁴ The failure to observe o-substituted products in the case of diphenylnitroxyl suggests that the phenyl group provides greater steric hindrance than does the *t*-butyl group, though the greater possible charge delocalisation in the diphenylnitrenium ion (280) may be an influencing factor.



C. 2 Decomposition of tetraz-2-enes

An additional test of the Cadogan-Rowley mechanism, a study of the thermolysis and photolysis of 1,4-di-*t*-butyl-1,4-bisphenyltetraz-2-ene, was carried out. It was known that both thermolysis and photolysis of this compound in cumene solution gave N-*t*-butylanilino-radicals¹⁵⁵ (scheme 180) identical to the intermediate postulated in the deoxygenation of N-*t*-butylphenylnitroxyl, therefore the thermolysis of the tetrazene in methanol or ethanol was expected to give comparable results.

As shown in Table 10 (Experimental section, p. 173) this proved to be the case. In methanol, in the absence of lithium chloride, thermolysis of the tetrazene gave N-*t*-butylaniline (23.7%) in addition to the ortho and para N-*t*-butylmethoxyanilines, (0.7 and 2.6%, respectively). The deoxygenation of the corresponding nitroxyl gave N-*t*-butylaniline plus the two N-*t*-butylmethoxyanilines in rather better yields;



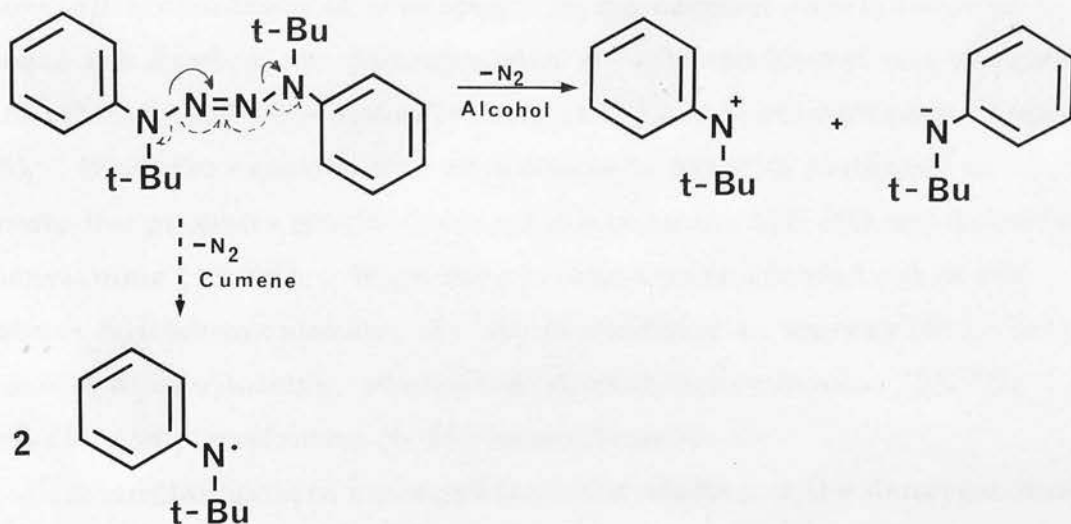
Scheme 180

ortho, 2.3% and para, 15.2%.¹²⁹ In this latter reaction the isomer ratio $\underline{p}:\underline{o} = 6.6:1$ is the same as that obtained from Gassman's authentic nitrenium ion source,¹³⁴ N-chloro-N-t-butylaniline, whereas the tetrazene route gives an isomer ratio $\underline{p}:\underline{o} = 3.7:1$. However in view of the small yields obtained from the tetrazene reaction, the appearance of the methoxylated compounds is of greater significance than the isomer ratio, which is subject to measurement errors.

Thermolysis of the tetrazene in methanol or ethanol in the presence of lithium chloride gave, as before, N-t-butylaniline (24%), but alkoxyanilines were only formed in trace amounts. The ring-chlorinated products, however, N-t-butyl-o-chloroaniline (0.2-0.8%) and N-t-butyl-p-chloroaniline (1.7-2.1%), were obtained. Deoxygenation of the corresponding nitroxyl gave, in methanol in the presence of lithium chloride, N-t-butylaniline (7.7%), N-t-butyl-o-chloroaniline (0.9%) and N-t-butyl-p-chloroaniline (5.2%), whereas in ethanol in the presence of lithium chloride the same three compounds were obtained (37.0, 4.4, and 18% respectively) in addition to N-t-butyl-o-ethoxyaniline (0.8%) and N-t-butyl-p-ethoxyaniline (4.6%). Thus the same pattern of products emerges from both tetrazene thermolyses and nitroxyl

deoxygenations, although the considerable variation in overall yields remains unexplained.

A possible criticism of the comparison of the data from tetrazene decompositions and nitroxyl deoxygenations is that the thermolysis of 1,4-di-*t*-butyl-1,4-bisphenyltetraz-2-ene to give N-*t*-butylanilino-radicals has previously been confirmed in cumene, but not in alcohol. Indeed it is possible to imagine that in a polar solvent, heterolytic fission of the tetrazene may occur (scheme 181). However, should this be the



Scheme 181

case, a nitrenium ion would be formed directly, and so the identification of ring-substituted anilines from the thermolysis of the tetrazene in alcohol may still be used as evidence in support of a nitrenium ion mechanism for the deoxygenation of N-*t*-butylphenylnitroxyl.

An earlier study¹⁹¹ of the photodecomposition of 1,4-dialkyl-1,4-bisphenyltetraz-2-enes in methanol or *t*-butanol showed that about eight unidentified, coloured compounds were produced. It has now been shown that 1,4-di-*t*-butyl-1,4-bisphenyltetraz-2-ene undergoes photodecomposition in methanol to give N-*t*-butylaniline (38.1%) and N-*t*-butyl-*o*-methoxyaniline (0.7%). When the experiment was repeated in the presence of lithium chloride, N-*t*-butylaniline (46%) and N-*t*-

butyl-p-methoxyaniline (0.6%) were obtained. The yields of methoxyanilines are too small to assume any significance, except to indicate that variations in conditions for thermolysis and photolysis of the tetrazene may be affecting the reaction pathway.

C.3 Solvent effects.

During the course of the study of the nitroxyl deoxygenations it was noted that substitution of ethanol for methanol as solvent increased the overall accountancy of products. In the original experiments of Cadogan and Rowley, the deoxygenation of diphenylnitroxyl was carried out in ethanol, and gave diphenylamine (65%) and 4-ethoxydiphenylamine (19%). When the reaction was re-examined, but with methanol as solvent, the products obtained were diphenylamine (23.2%) and 4-methoxydiphenylamine (13.7%). When the reactions were carried out in the presence of lithium chloride, the use of methanol as solvent led to only a trace of diphenylamine, whereas in ethanol, diphenylamine (31.2%) and 4-chlorodiphenylamine (6.5%) were obtained.

A similar pattern emerged from the studies of the deoxygenation of N-t-butylphenylnitroxyl (see Table 9, Experimental section, p. 171). When the reaction was carried out in methanol the products were N-t-butylaniline, N-t-butyl-o-methoxyaniline (2.3%), and N-t-butyl-p-methoxyaniline (15.3%),¹²⁹ whereas in ethanol the products were N-t-butylaniline (20.5%), N-t-butyl-o-ethoxyaniline (5.6%), and N-t-butyl-p-ethoxyaniline (41.4%). In the presence of lithium chloride, in methanol, N-t-butylaniline (7.7%), N-t-butyl-o-chloroaniline (0.9%), and N-t-butyl-p-chloroaniline (5.2%) were obtained, but in ethanol the accountancy increased to give N-t-butylaniline (37.0%), N-t-butyl-o-chloroaniline (4.4%), N-t-butyl-p-chloroaniline (18.0%), N-t-butyl-o-ethoxyaniline (0.8%), and N-t-butyl-p-ethoxyaniline (4.6%).

A possible reason for this variation with solvent is the increased acidity of methanol relative to ethanol [pK_a (MeOH) = 16, pK_a (EtOH) = 18],¹⁹² however, when the deoxygenation of N-t-butylphenylnitroxyl was carried out in ethanol, the addition of acetic acid made no significant

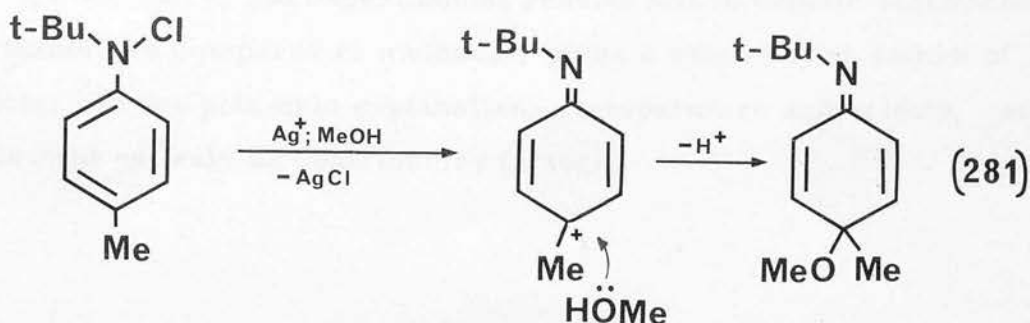
change in the product yields (see Table 9). When lithium chloride was added to the ethanol, the presence of a small quantity of trifluoroacetic acid resulted in a significantly reduced yield of N-t-butylaniline (12.0%, cf. 37.0% in the absence of acid), but an increased yield of N-t-butyl-o- and p-ethoxyanilines (3.1 and 15.5% respectively, cf. 0.8% and 4.6%). It was shown in a control experiment that CF_3COOH did not catalyse the ethoxylation of N-t-butylaniline. The yields of N-t-butyl-o- and p-chloroanilines produced in the same reaction were very slightly reduced (3.5 and 14.6% respectively, cf. 4.4 and 18.0%).

Another possible explanation for the variation in product yields is the difference in boiling points of methanol (65.0°) and ethanol (78.5°). To check this possibility the deoxygenation of N-t-butylphenylnitroxyl was carried out in ethanol, but at 65°. Lithium chloride was included in the reaction mixture, and the expected products were obtained. The yields of N-t-butylchloro- and ethoxy-anilines were not significantly affected by the change in reaction temperature, but the yield of N-t-butylaniline was greatly reduced (see Table 9).

Experiments designed to examine the combined effects of a lower reaction temperature and the addition of CF_3COOH gave inconsistent results. In one case the yield of N-t-butylaniline was unaffected by the changed conditions, whereas the yields of substituted products were decreased, but in another experiment the yields of N-t-butylaniline and chlorinated anilines were reduced, but the yields of ethoxyanilines increased (see Table 9).

C.4 Deoxygenation of N-t-butyl-p-tolynitroxyl

The deoxygenation of N-t-butyl-p-tolynitroxyl was examined because Gassman¹³⁴ had shown that the silver-ion catalysed solvolysis of N-t-butyl-N-chloro-p-methylaniline gave 4-methyl-4-methoxy-2,5-cyclohexadienone N-t-butylimine (281) which was cited as good evidence for the proposed nitrenium ion mechanism (scheme 182). However, neither the imine, nor the corresponding cyclohexadienone (a hydrolysis product of the imine), could be identified in the final deoxygenation reaction mixture.



Scheme 182

C.5 Conclusions

These studies have further confirmed that an aryl nitrenium ion is formed during the deoxygenation of diphenylnitroxyl and N-t-butylphenylnitroxyl by triethyl phosphite in alcohol solution. In addition, minor changes in the structure of the solvent have considerable influence on the overall yields of identified products (anilines), but the reason for this is not clear. There are several stages in the proposed mechanism (scheme 179):- radical attack of the nitroxyl on the phosphorus reagent; fission of the phosphoranyl radical; electron-transfer between aminyl radicals; nucleophilic attack of the solvent molecule on the aryl nitrenium ion; and the final rearomatisation. It is conceivable that most of these steps could be influenced by temperature and acidity of the solvent, but in the experiments carried out in ethanol at reduced temperature or with increased acidity, which attempted to mimic the conditions incurred by the use of methanol, the overall yields of nitrenium ion-derived products dropped significantly only when the effects were combined, and in this case the results were not reproducible.

Variations in the yields of N-t-butylaniline are more complex, probably because this compound can be derived by two routes viz. hydrogen abstraction by the N-t-butylanilino-radical and proton

abstraction by the N-t-butylnilino-anion (see scheme 179).

In summary, the experimental results fail to explain satisfactorily why ethanol, as compared to methanol, gives a much better return of products, but two plausible explanations, temperature and acidity, cannot be ruled out entirely as contributory factors.

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The Reactivity of Organophosphorus Compounds. Part 33.¹ Formation of
Stable 3,4-Diaryl-4,5-dihydro-2-oxo-1,2,5-oxazaphosph(V)oles by Reaction of
1,2-Diaryl-1-nitroethenes with Phosphorus(III) Esters

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Reaction, in *t*-butyl alcohol at room temperature, of phosphorus(III) esters with (*E*)-1,2-diaryl-1-nitroethenes gives 1:1 adducts, the 3,4-diaryl-4,5-dihydro-2-oxo-1,2,5-oxazaphosph(V)oles (1) (Table) (Scheme). By ³¹P n.m.r. the conversions appeared to be quantitative, but isolated yields varied from 27 to 93%. These compounds were of interest as possible intermediates in the high temperature conversion of 1,2-diarylnitroethenes into 2-arylindoles by reaction with phosphorus(III) esters.² Key structural information was provided by ³¹P n.m.r. (negative chemical shifts, insensitive to changes in solvent polarity) and ¹H n.m.r. [coupling of α -hydrogen (H^a) to phosphorus, and temperature-dependent variation of signals corresponding to characteristic reorganisation (pseudorotation) of P–O–alkyl groups], all of which points to the pentaco-ordinate phosphorane system (1).

The stable oxazaphospholes (1) are related to the much less stable analogues isolated from corresponding reactions of all-aliphatic 1-nitroalkenes.³ Related oxazaphospholes have been postulated as intermediates in reactions of 1-phenyl-2-nitroethene with trimethyl phosphite⁶ and diphenylphosphinous chloride.⁷

Table 5,5,5-Trialkoxy- (and 5,5-dialkoxy-5-phenyl-3,4-diaryl-4,5-dihydro-2-oxo-1,2,5-oxazaphosph(V)oles (1)

| R ¹ | R ² | R ³ | R ⁴ | R ⁵ | Yield (%) | ³¹ P δ † |
|------------------------------------|-----------------|----------------|----------------|----------------|-----------|----------------------------|
| Me | H | H | H | MeO | 85 | –36.6 |
| Me | Cl | Cl | H | MeO | 27 | –42.7 |
| Me | Me | Me | Me | MeO | 37 | –38.6 |
| Me | MeO | MeO | MeO | MeO | 73 | –39.1 |
| Me | NO ₂ | H | H | MeO | 82 | –39.3 |
| Et | H | H | H | EtO | 48 | –37.6 |
| Et | Me | Me | Me | EtO | 34 | –40.5 |
| Me | H | H | H | Ph | 93 | Insoluble |
| Me | Cl | Cl | H | Ph | 92 | –33.6br |
| Me | Me | Me | Me | Ph | 54 | –24.5br |
| ·[CH ₂] ₂ · | H | H | H | Ph | 83 | –16.0 |
| | | | | | | –16.9 |

† Positive to high frequency.

Techniques used: ³¹P, ¹H N.m.r. spectroscopy

References: 9

Tables 1–4: Yields, m.p.s., analyses, and ³¹P and ¹H n.m.r. data for the oxazaphospholes

Table 5: Yields and m.p.s. of (*E*)-1,2-diaryl-1-nitroethene

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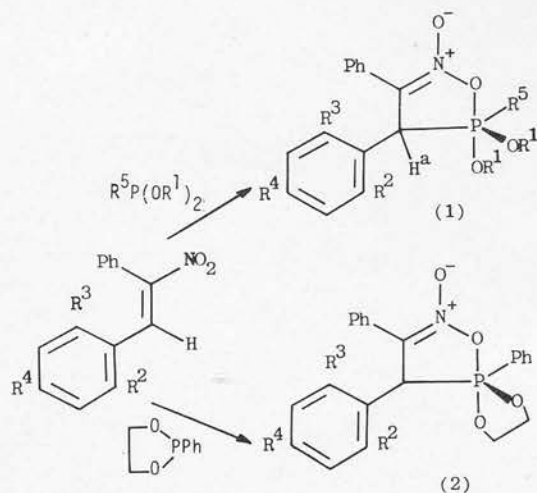
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Scheme

In those cases based on dimethyl phenylphosphonite (1; R⁵ = Ph R¹ = Me), diastereoisomers resulting from two possible equatorial positions of the *P*-phenyl group were detected by ³¹P and ¹H n.m.r. An even clearer example was provided by the oxazaphosphole (2) based on 2-phenyl-1,3,2-dioxaphospholan in which interchange of isomers involves a pathway of particularly high energy.